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# High Temperature Barrier Coatings for Refractory Metals

G.A. Malone and T. Walech  
*Electroformed Nickel, Inc.*  
*Huntsville, Alabama*

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METALS (Electroformed Nickel)  
133 p

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#### **IN MEMORIUM**

This work is dedicated to the memory of Mr. John Kazaroff of NASA Lewis Research Center. His inspiration and council were highly regarded by many friends and colleagues. He will never be forgotten.

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## SUMMARY

Improvements in high temperature oxidation resistant metal coating technology will allow NASA and commercial entities to develop competitive civil space transport and communication systems. The success of investigations completed in this program will have a positive impact on broadening the technology base for high temperature materials. The work reported herein describes processes and procedures for successfully depositing coherent oxidation barrier coatings on refractory metals to prevent degradation under very severe operating environments. Application of the new technology developed is now being utilized in numerous Phase III applications through several prominent aerospace firms.

Major achievements have included:

1. Development of means to deposit thick platinum and rhodium coatings with lower stress and fewer microcracks than could be previously achieved.
2. Development of processes to deposit thick adherent coatings of platinum group metals on refractory substrates that remain bonded through high temperature excursions and without need for intermediate coatings. Bonding processes unique to specific refractory metals and alloys have been defined.
3. Demonstration that useful alloys of refractory and platinum coatings can be made through thermal diffusion means.
4. Demonstration that selected barrier coatings on refractory substrates can withstand severe oxidizing environments in the range of 1260° to 1760°C for long time periods essential to the life requirements of the hardware.
5. Successful application of the processes and procedures to prototype hardware.

The results of these studies have been instrumental in improved thermal oxidation barrier coatings for the NASP propulsion system. Other Phase III applications currently being exploited include small uncooled thrustors for spacecraft and microsatellite maneuvering systems.

## INTRODUCTION

The purpose of this work is the support of NASA's technology base for innovative advances in gas turbine engine materials and structures to enable the development of highly competitive transport propulsion systems into the next century. To satisfy these needs, the material system must have reasonably low weight, increased temperature capability, and improved reliability and life span. Such systems have a great many commercial applications such as heat exchangers for future aerospace vehicles where high mach velocities generate tremendous thermal energy which has to be channeled for dissipation, furnace components, liquid metal handling systems, thermocouples, thermoelectric devices, and high temperature engineering structures.

Phillips [1] has noted that "what we can accomplish and what can be made to operate at temperatures above 3000°F are directly related to the materials available for use and how long the materials are stable in the environment of interest". Unfortunately, the list of available materials must decrease as the temperature of utilization increases. The stability of materials on such a list is a function of other materials present and the atmospheric conditions that prevail. Phillips defined the high temperature stable elements in groupings as (1) the noble metals, (2) the refractory metals, (3) carbon and boron, and (4) miscellaneous elements.

Phillips considered only iridium, rhodium, platinum, palladium, and alloys of these elements as suitable for use in high temperature oxidizing environments. Data for these metals is shown in Table I. He noted that ruthenium and osmium react with oxygen to form volatile MO type oxides. Platinum and rhodium, as well as platinum and iridium alloys, are widely used and offer the best service up to 1800°C (3270°F). Iridium can be

used to higher temperatures, but its rate of volatility becomes appreciable. Iridium is usually brittle and difficult to fabricate, while palladium is also brittle and has the lowest melting temperature of the platinum group metals. The platinum group (or noble) metals have another feature that is advantageous in coating - most of them can be electrodeposited.

Phillips also considered the refractory metals for high temperature service and listed their properties of interest in Table II. This group includes the highest melting temperature metals known; however, they are susceptible to oxidation at high temperatures. Some of the metals in this group can be alloyed to develop oxide

TABLE I Noble Metals and Intrinsic Properties			
Metal	Melting Pt. °F   °C	Atomic Radius Å	Density g/cc
Os	4890 (2700)	1.336	22.5
Ir	4430 (2443)	1.352	22.4
Ru	4350 (2400)	1.322	12.2
Rh	3560 (1960)	1.342	12.4
Pt	3220 (1769)	1.380	21.5
Pd	2825 (1552)	1.370	11.9

skins giving partial protection at high temperatures, but this skin continues to grow with the presence of oxygen. The useful life of the alloy is limited by the amount of skin that can be tolerated and the rate at which oxygen is available for skin growth. Use of refractory metals has been advanced by the development of chemical techniques to produce metallic compound skins

such as silicides and aluminides to act as barrier layers to oxygen diffusion. However, these coatings do not result in a lasting protection at temperatures approaching 2000°C (3600°F). Many such coatings also have poor thermal conductivity or inadequate thermal cycling life due to poor ductility (brittleness).

In considering the carbon and boron grouping, Phillips noted that carbon was in a class by itself. It is the only material that has an increasing strength-to-density ratio in the temperature range of 2400° to 4400°F. Carbon based materials are like the refractory metals in that they are readily oxidized in oxidizing environments at high temperatures. Carbon and graphite products provide excellent service in neutral or reducing environments (or vacuo) at temperatures up to 4000°F. Boron is a high-melting metal which is difficult to obtain in pure form. It is hard and difficult to fabricate and oxidizes readily to form volatile oxides at moderate temperatures. It is not widely used other than as filaments for strengthening composites where less severe temperatures are involved. Among the miscellaneous elements, lutetium melts at 1530°C (2770°F) and technetium melts at 2700°C (4890°F). Both are very reactive and burn in oxidizing atmospheres.

Chelius [2] reviewed materials for high temperature applications in the chemical industry. He defined refractory metals as those having melting points higher than 2000°C (3632°F) and placed ten metals in this category: tungsten, molybdenum, columbium, boron, hafnium, ruthenium, osmium, rhenium, and iridium. Four of these metals - tungsten, molybdenum, tantalum, columbium, and alloys of these metals have undergone amazing development and utilization. All four metals are body-centered-cubic in crystal structure. The general properties of tungsten and molybdenum are similar to each other, as are the similarities between tantalum and columbium. Tantalum and columbium are (1) easily cold worked, (2) have high solubility capacity for hydrogen, oxygen, and nitrogen,

Metal	Melting Point		Density g/cc	Thermal Conductivity	Thermal Expansion	Specific Heat-cal/ g °C
	°F	°C		cal/sec. cm. °C	micro-inch/ inch °C	
Tungsten	6152	3400	19.3	0.399	4.45	0.034
Tantalum	5425	2996	16.6	0.130	6.5	0.036
Molybdenum	4752	2622	10.2	0.349	5.45	0.065
Columbium	4379	2415	8.57	0.125	7.1	0.065
Hafnium	3866	2130	13.09	0.053	6.2	0.035
Vanadium	3452	1900	6.11	0.074	8.3	0.120
Zirconium	3326	1830	6.5	0.21	5.7	0.066
Chromium	2882	1550	7.14	0.16	5.0	0.107

(3) have low brittle-ductile transformation temperatures, and (4) are relatively insensitive to strain rates. Chelius confirmed the poor oxidation resistance of these metals at high temperatures.

Barto and Hurd [3] discussed refractory metals in liquid metals handling, a matter of concern when such devices are internally cooled with fluids such as liquid sodium. They point out that (1) the thermal expansion of refractory metals is low, (2) none of the refractory metals has an allotropic phase change below the melting point, and (3) tantalum and columbium have about the same thermal conductivity as iron, while molybdenum and tungsten are about three times better, Table III.

TABLE III - REFRACTORY METAL PROPERTIES

Wimber [4] authored an extensive study to develop some protective coatings for tantalum based alloys under a contract supported by the Air Force Materials Laboratory. The purpose of this work was the protection of tantalum based alloys from oxidation at temperatures of 1650° to 2200°C. They observed that alloy additions

	Molybdenum	Tungsten	Tantalum	Columbium	Iron	Nickel	Copper
Melting Point ....	2610°C	3410°C	2996°C	2468°C	1536°C 2790°F	1453°C 2647°F	1083°C 1981°F
Density — gr/cm <sup>3</sup>	10.22	19.3	16.6	8.57	7.87	8.90	8.96
lb/in <sup>3</sup>	0.369	0.697	0.600	0.31	.284	.322	.324
Specific Heat ....	0.066	0.033	0.034	0.065	0.11	0.105	0.092
Thermal Conductivity							
CAL/sq							
cm/cm/sec/°C ...	0.34	0.397	0.130	0.125	0.18	0.22	0.941
BTU/hr/ft/°F ....	82.1	96.6	31.2	30.1	40	53	225
Thermal Expansion							
Micro — in/in°C	4.9	4.6	6.5	7.31	11.76	13.3	16.5
Micro — in/in°F	2.7	2.55	3.6	4.06	6.53	7.39	9.20

of rhodium and platinum appeared to improve the oxidation resistance of iridium which, even in the unalloyed condition, demonstrated a resistance to the ingress of oxygen greater than the resistance of Hf-25Ta alloy for oxidation in flowing dry air. Diffusional compatibility studies were made for the Hf-HfO<sub>2</sub> and IrW systems.

Gadd [5] reported results of an Air Force Materials Laboratory contract to advance protective coatings for tantalum and columbium alloys. Areas investigated included development of metallic coatings for oxidation protection to temperatures of 3500°F. The use of rhenium has received considerable attention as a refractory material due to its high melting point of 3180°C (5755°F); this is second only to tungsten. It also exhibits an intriguing combination of physical, chemical, and metallurgical properties at room temperature and under cryogenic conditions. It imparts a number of these properties to its alloys. It is most commonly alloyed with molybdenum or tungsten to improve the ductility of the alloyed component.

Cramer [6] and coworkers at the Bureau of Mines investigated the

electrodeposition of thick coatings of platinum and palladium on refractory metals from aqueous electrolytes. Their goal was to develop thick, adherent, and coherent coatings on substrates of industrial and engineering importance. Pretreatment procedures for columbium, copper, graphite, molybdenum, nickel, stainless steel, tantalum, titanium, tungsten, vanadium, and zirconium substrates were studied. New pretreatment procedures for columbium, molybdenum, stainless steel, tantalum, tungsten, and nickel were developed. This work was reported in 1967.

Beach and Gurklis [7] authored a 1959 survey of procedures for electroplating coatings on refractory metals which included vanadium, columbium, tantalum, tungsten, titanium, and molybdenum. They cited the advantages and disadvantages of electroplating (or electrocladding) as:

#### Advantages

- (1) Cladding thickness could be achieved that was not attainable by wrought cladding methods.
- (2) Coating could be applied without heat or stress.
- (3) Can be used to coat irregular shapes.
- (4) Can be used to apply multimetal layers.

#### Disadvantages

- (1) There is a tendency towards porosity typical of crystal structure.
- (2) Electroplate structure and quality is influenced by surface state of the basis metal.
- (3) There is a need to change electrical contact area to avoid uncoated spots.

Passmore and coworkers [8] investigated diffusion barriers for refractory metals at the Manufacturing Laboratories of Wright-Patterson Air Force Base in 1960. Twenty-three base-barrier combinations of metals were screened by annealing diffusion couples at 1700°C. From metallographic examination, hardness measurements, and electron beam analysis, it was concluded that hafnium and iridium would be the most promising barriers for tungsten at 1700°C. Iridium was considered the best choice for coating tantalum and molybdenum.

It was evident that most work to coat oxidation protection barriers on refractory metals was performed over thirty years ago, and few, if any, continuation studies have been made.

**TASK I - INVESTIGATION OF PULSED CURRENT DEPOSITION  
OF OXIDATION RESISTANT NOBLE METALS  
PART A - PLATINUM AND RHODIUM ELECTRODEPOSITS**

**Platinum - State of the Art**

Lowenheim [9] notes the value of platinum for protecting refractory metals from high temperature oxidation. Significant platinum plating baths are based on ammine, nitrilo, and hydroxo complexes or on acid chloride. Some typical formulations are listed by Lowenheim in Table IV.

**TABLE IV - BATHS FOR PLATINUM PLATING**

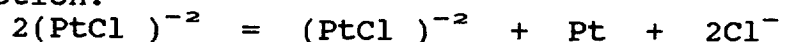
Bath:	Concentrations, g/L				
	R	S	T	U	V
Source of Pt	"P" salt	"P" salt	$H_2Pt(NO_3)_2SO_4$	$K_2Pt(OH)_2$	$H_2PtCl_6$
Pt, as metal	10	40	5	12	20
Ammonium nitrite, $NH_4NO_2$	100				
Sodium nitrite, $NaNO_2$	10				
Ammonia, $NH_3$ , 28%	40				
Sulfamic acid, $NH_2SO_3H$		80			
Sulfuric acid, $H_2SO_4$			to pH 2		
Potassium hydroxide, KOH				15	
Hydrochloric acid, HCl					300
Temperature, °C	90	75	40	75	65
Current density, A/m <sup>2</sup>	40	150	50	75	—

Indira and coworkers [10] examined effects of cetyltrimethylammonium bromide in alkaline platinum baths and claimed more uniform deposition. Walters and coworkers [11] studied adhesion and hardness of platinum coatings deposited from molten salts on substrates that included TZM, a molybdenum alloy. Fracture loads of 30 to 68 ksi were reported. Sexton and Clifford [12] reported electroforming one micron thick platinum screens using a commercial low-stress platinum bath at 80°C with agitation and a current density of 14 amps/ft<sup>2</sup>. The bath used was a Sel-Rex Platanex III bath containing 10 g/l platinum as a tetraamineplatinum sulfamate complex.

Baumgartner and Raub [13] reviewed electrodeposition of platinum, including work in their laboratories up to about 1988. They note that research on the electrodeposition of platinum has been quite neglected in recent years. Generally, the published literature contains only broad statements about the bath composition, and information is lacking on the preparation of the bath, its operation, and the properties of the deposits obtained. They advise that electrolytes may be divided into two groups: (a) baths containing platinum in the divalent state and (b) those with it in

the tetravalent state. In the selection of the platinum plating baths for the studies reported herein, comments of these investigators was given careful consideration. Baumgartner and Raub organized the more significant platinum solutions by type, composition, and operating conditions as shown in Table V.

Deposits from the acid chloride baths, with or without citrate complexing, tend to be fine grained but irregular. Under carefully controlled conditions, this solution produces crack-free, ductile crystalline layers up to 20  $\mu\text{m}$  in thickness. These baths tend to be fairly unstable and have short useful lives. They are also very corrosive, and many substrate materials must be protected by intermediate coatings. A major problem occurs with these baths in that chloride ion builds up with use, generating discolored deposits. Although platinum salts in these baths are tetravalent (+4), they are considered to be divalent because  $\text{Pt}^{+4}$  ion is cathodically reduced to  $\text{Pt}^{+2}$  according to the equilibrium reaction:



At high concentrations of hydrochloric acid, the equilibrium is strongly shifted to the left side of the equation.

In dinitrodiammine-based platinum baths, the divalent platinum ion is stabilized by complexing it with amino compounds to prevent oxidation to tetravalent platinum. The source of platinum ion in this bath is cis-dinitrodiammineplatinum which is usually called platinum-p-salt. In a simple form, Bath A of Table V, the electrolyte reacts irregularly due to changes in the nitrite concentration which influences dissociation of the platinum complex and decreases plating efficiency. The bath can be replenished by frequent additions of Pt-p-salt, but its levelling power is fairly poor. The quality of the deposits is largely dependent on the concentration of platinum in the bath - the higher the concentration, the better the deposits.

Baumgartner and Raub also noted that deposits from the Pt-p-salt bath could be improved by periodically reversing the 5 to 6  $\text{A}/\text{dm}^2$  current using a 5 second forward and 2 second reverse cycle. A platinum deposition rate of 5  $\mu\text{m}$  per hour was obtained. They assumed that this depolarization of the cathode also reduced porosity in the platinum, since a 5  $\mu\text{m}$  deposit over nickel withstood boiling hydrochloric acid for five hours with no weight loss. Other modifications of the Pt-p-salt bath are shown in Table V as means for improving ductility, porosity, current efficiency, and appearance.

These investigators describe electrolytes of dinitrosulfatoplatinous acid as free of ammonia or amines. They are based on the complex  $\text{H Pt}(\text{NO}) \text{SO}_4$ . It is possible to coat a wide range of substrates with these electrolytes without having to plate an intermediate layer of protective metal. The advantages of the DNS

**Table IVB**  
**Baths for Platinum Electrodeposition**

Type of bath Reference	Chloride	Dinitrodiammineplatinum						DNS	Alkali hexahydroxyplatnates				Phosphate
		A	B	C	D	E	F		A	B	C	D	
		Concentrations, g/l											
Chloroplatinic acid $H_2PtCl_6$	10-50												
Ammonium hexachloro- platinate $(NH_4)_2PtCl_6$	15												
Platinum-p-salt $Pt(NH_3)_2(NO_2)_2$		8-16.5	20	6-20	8	6-20	16.5	10					
Dinitrosulphato- platinous acid $H_2Pt(NO_2)_2SO_4$													
Sodium hexahydroxy- platinate $Na_2Pt(OH)_6 \cdot 2H_2O$									20	18.5	20		
Hexahydroxyplatonic acid $H_2Pt(OH)_6$												20	
Potassium hexahydroxy- platinate $K_2Pt(OH)_6$													7.5
Platinum chloride $PtCl_4 \cdot 5H_2O$													
Ammonia (28%) $NH_3$		50											
Hydrochloric acid $HCl$	180-300												
Sodium citrate $Na_3C_6H_5O_7 \cdot 2H_2O$	100												20-25
Ammonium chloride $NH_4Cl$	4-5												
Ammonium nitrate $NH_4NO_3$		100											
Sodium nitrite $NaNO_2$		10											
Fluoroboric acid $HBF_4$			50-100										
Sodium fluoroborate $NaBF_4$			80-120										
Sulphamic acid $NH_2SO_3H$				20-100									
Phosphoric acid $H_3PO_4$					80	10-100		pH 2					
Sulphuric acid $H_2SO_4$						10-100	70						
Sodium acetate $NaCH_3COO$							100						
Sodium carbonate $Na_2CO_3$									10	5.1			
Sodium hydroxide $NaOH$										5.1			
Sodium oxalate $Na_2C_2O_4$										30.8	15		
Sodium sulphate $Na_2SO_4$													20
Potassium hydroxide $KOH$													100
Diammonium hydrogen phosphate $(NH_4)_2HPO_4$													
Disodium hydrogen phosphate $Na_2HPO_4$													
Potassium sulphate $K_2SO_4$												40	
Temperature, °C	45-90	80-90	90-95	70-90	65-100	75-100	80-90	30-70	75	65-80	75	70-90	70-90
Current density, A/dm <sup>2</sup>	2.5-3.5	0.5-1.0	0.3-2.0	2-5	0.2-2	0.5-3.0	0.5	2.5	0.8	0.8	0.75	0.3-1	0.3-1
Current efficiency, per cent	15-20	70	10	14-18	15	15	35-40	10-15	100	80	100	10-50	10-50



bath are claimed to be (1) bright and smooth deposits, (2) baths are stable and produce constant results, and (3) thicknesses to 25  $\mu\text{m}$  can be produced. However, cracks form at greater thicknesses.

A group of alkaline platinum electrolytes are shown in Table V under the heading of alkali hexahydroxyplatinate. These usually contain sodium or potassium salts of hexahydroxyplatonic acid and sodium or potassium hydroxide to provide a pH of about 13. Some claimed advantages of these baths are high current efficiency (100 percent), deposits are dense and bright (for fresh electrolytes), ease for regeneration, and nickel or stainless steel anodes may be used. A disadvantage lies in the stability of the baths. It was claimed that oxalate, sulfate, or acetate additions would improve stability, but others dispute this on the basis that there was an increased tendency for precipitation of insoluble platinum compounds.

Baumgartner and Raub reference phosphate based baths for deposition of platinum, Table V. Platinum (IV) in the form of chloro compounds such as platinum (IV) chloride, dihydrogen hexachloroplatinate (chloroplatinic acid), and alkali salts of this acid are generally used. Alkali and ammonium phosphates are added to improve conductivity, the latter supposedly enhancing deposition. Current efficiencies to fifty percent and deposit thicknesses to 0.5  $\mu\text{m}$  are reported. High integrity foils and tubes can be produced from such baths. The bath is reportedly difficult to prepare and the presence of ammonium phosphate is critical to improved dissolution of an  $(\text{NH}_4)^+$  containing platinum complex in the bath.

### Platinum Plating Efficiency Studies

Plating in these studies was from one liter baths in beakers on hotplates equipped with magnetic stirrers, Figure 1. Each hotplate could be programed to control temperature and stirring speed. Current for all plating runs was supplied by two Kraft Dynatronics Model DPR-20-30-100 power supplies. These units can supply pulsed or direct current, with or without periodic current reversal. The average current capacity of each unit is 30 amperes, while the peak current density possible is 100  $\text{A}/\text{ft}^2$ . Times can be set in seconds or milliseconds with ranges of each from 0.1 to 99.9. A ratio of forward to reverse timing with independent currents can be set for periodic current reversal. However, there are some special rules to be followed in setting forward and reverse cycles due to the fact that cycles must be in whole integers for a time span. An illustration of a typical power supply is found in Figure 2. A precaution must be taken in using pulsed current deposition in that impedance in the wiring leads and capacitance in the plating bath can dampen the current pulses so that the nulls are adversely affected. This must be

overcome by twisting the positive and negative leads to counter impedance and placing the cathode as close as practical to the anode to reduce capacitance of the solution.

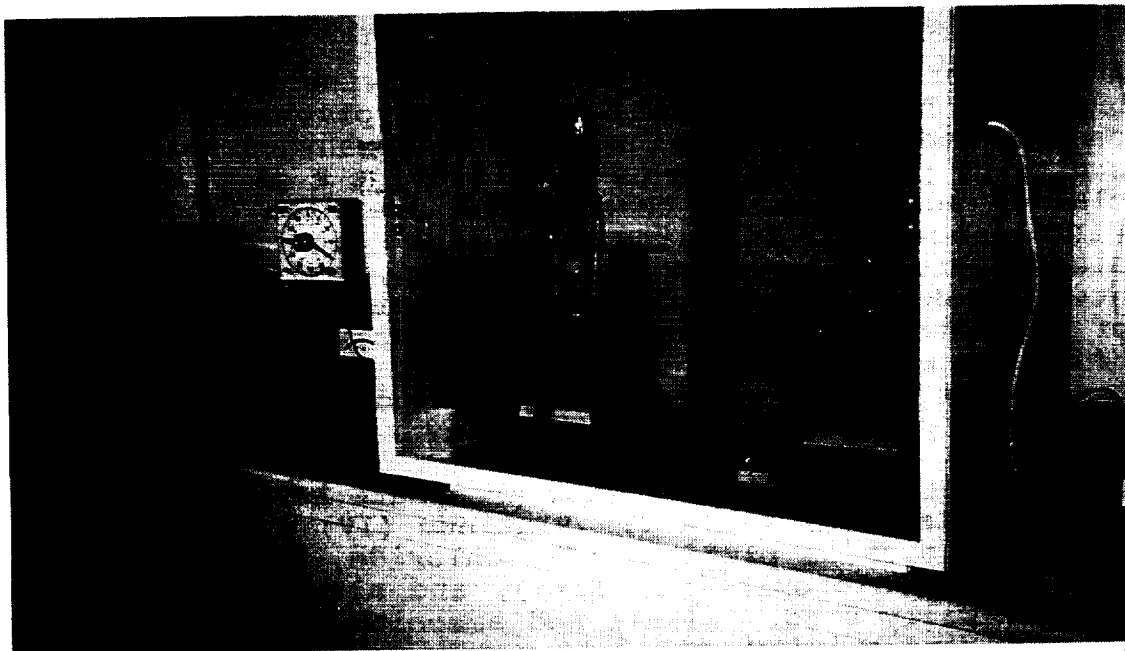


Figure 1. Physical Layout of Platinum Electroplating Facility.

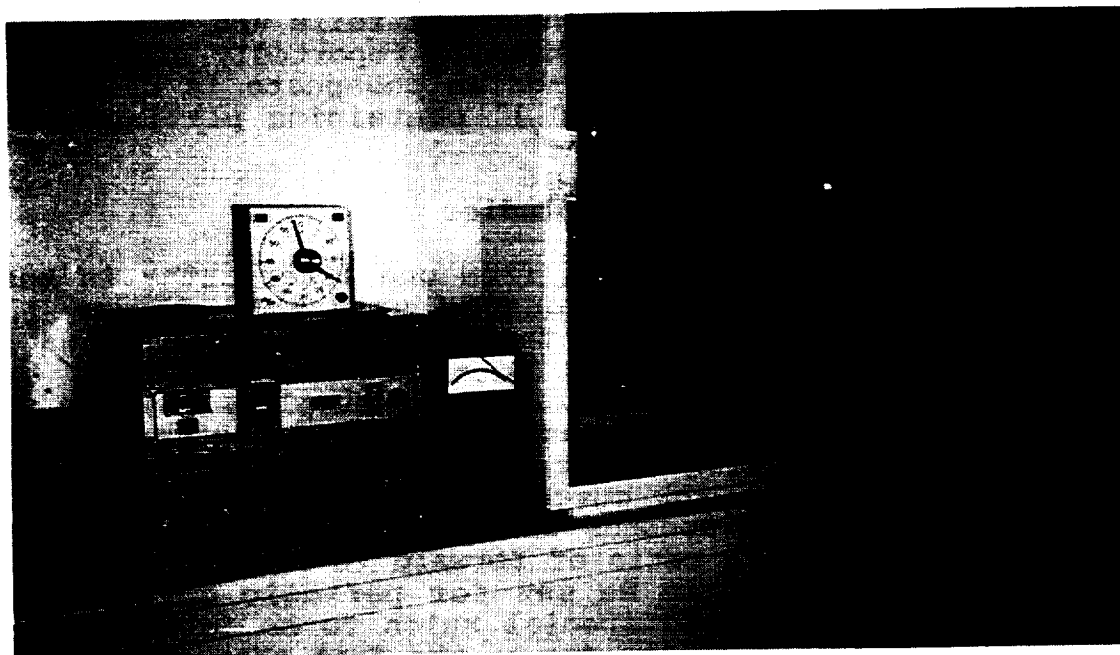


Figure 2. Illustration of Pulse/Pulse Periodic Reverse Power Supply for Noble Metal Plating Studies.

The plating baths were contained in a fume hood to minimize atmospheric contamination. Anodes were platinized titanium. From

Figure 2, a Yokogawa ammeter is visible next to the power supply. This instrument is a calibrated primary standard used to verify the average current output in the forward direction. It is essential that such current confirmation be made where small currents are used on a high capacity power source. Reversing the ammeter leads enables verification of reverse current in the PR (periodic reverse) mode.

The substrate specimens were OFHC copper tubing, 2.54 cm (1 in) outside diameter, cut to a length of 1 inch. Outside ends were sanded on a lathe to remove high current density areas. Each of the specimens was chemically deoxidized in a copper bright dip solution and activated cathodically in sulfuric acid for nickel plating in a standard nickel sulfamate bath without additives other than wetting agent. The nickel plated samples were then plated with a gold strike using Technic Orostrike gold. The purpose of these pretreatments was the inhibition of corrosion of the substrates from highly reactive noble metal plating baths and the possibility of chemical attack through pores in preliminary thin coatings. Special protective measures were required to assure that all noble metal plating was confined to designated outside surfaces of the gold plated tube surfaces. Each tube section was mounted on a shaft for rotation during plating. Internal contact from the shaft to the substrate was made by copper strips under spring load. Shaft to substrate standoff was achieved by Teflon spacers at each end of the substrate tube. The entire specimen mounting is shown in Figure 3, as well as a number of gold plated substrates.

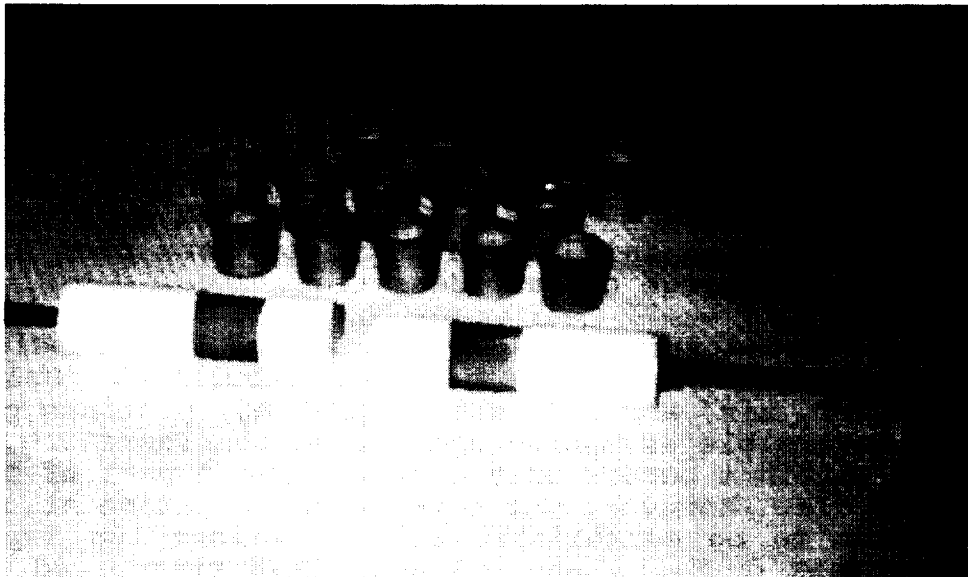


Figure 3. Gold Plated Tubular Substrates and Fixturing for Platinum Plating Studies.

The Sel-Rex Platanex III electrolyte was used for the plating efficiency studies based on prior experience with thick deposition. Although proprietary, this bath is believed to be of the diammino dinitroplatinum (II) sulfamate family. Operating particulars are given by the supplier as:

	Nominal	Range
Platinum	12 g/l	8-12 g/l
pH	1.5	1.3-1.8
Temperature	80°C (175°F)	75-85°C (165-185°F)
Anode/Cathode Ratio	1 to 1 or Higher	
Cathode Current Density	20 ASF	10-30 ASF
pH Adjustment	Raise with Ammonium Hydroxide Lower with Sulfamic Acid	
Anodes	Platinized Titanium or Equivalent	
Platinum Replenishment	Concentrate Additions	

A test matrix was devised for evaluating effects of direct current, pulsed current, and pulsed PR on plating efficiencies and deposit visual quality. Table VI lists electrodeposition conditions, deposit weights obtained, and calculated plating efficiencies for the Platanex III platinum electrolyte. All peak forward and peak reverse current densities were based on settings of mechanical dials and assume that the true peak current and the setting values are the same. This is not truly correct, since calibration of non-pulsed settings against a calibrated ammeter showed results that differed up to twenty percent at low current. This is not unexpected because of the high current capacity of the power supply and the fact that the peak current dial adjustments are in 0.1 ampere increments.

These current variances were not considered crucial in this exercise, since the qualitative effects of pulse manipulation on current efficiency and deposit appearance were of interest. As the pulse was applied and combinations of forward and periodic reversed pulse utilized, the readings of an in-line calibrated ammeter of very high precision were of questionable accuracy due to dampening effects. On this basis, the peak current approximations from the mechanical dial settings were used and calculations made of average current densities.

It will be noted that total cycle plating efficiencies and forward current plating efficiencies are tabulated. Unlike copper, zinc, silver, tin, and gold electroplating, platinum group metals are not reversible as anodes and cathodes. Therefore, all deposition of platinum occurs only on the forward part of the periodic reverse cycle. However, the reverse polarization allows chemical equilibrium to be established after platinum ion depletion from the high peak currents and voltages that transpired in the forward current direction. Therefore, efficiencies were determined based on (1) total plating time and (2) the forward plating time only.

TABLE V - PLATINUM PLATING EFFICIENCY STUDY

SPECIMEN NUMBER	SEL-REX PLATANEX III PLATINUM PLATING EFFICIENCY STUDIES													
	DIRECTION TIME	FORWARD PULSE	REVERSE PULSE	PEAK CUR. DENS. (Amp/Dm <sup>2</sup> )	FORWARD CUR. DENS. (Amp/Dm <sup>2</sup> )	PEAK REVERSE CUR. DENS. (Amp/Dm <sup>2</sup> )	CALCULATED AVERAGE CUR. DENS. (Amp/Dm <sup>2</sup> )	PLATING TIME (Minutes)	DEPOSIT WEIGHT (Grams)	WEIGHT AT 100% EFFICIENCY (Grams)	TOTAL CYCLE	FORWARD CURRENT PLATING EFF. (%)		
1	Fwd.Only	DC Only	Fwd.Only	1.110	1.110	0.000	1.110	16.00	0.0858	0.2185	39.3	39.3		
2	Fwd.Only	DC Only	Fwd.Only	2.217	2.217	0.000	2.217	8.00	0.0826	0.2185	37.8	37.8		
3	Fwd.Only	DC Only	Fwd.Only	3.374	3.374	0.000	3.374	5.33	0.0601	0.2184	27.5	27.5		
32	Fwd.Only	0.3/0.1	Fwd.Only	3.861		0.000	2.896	24.00	0.0837	0.3132	26.7	26.7		
4	Fwd.Only	0.1/0.9	Fwd.Only	18.448		0.000	1.845	16.00	0.0734	0.3637	20.2	20.2		
5	Fwd.Only	0.3/0.9	Fwd.Only	6.864		0.000	1.716	16.00	0.0703	0.3384	20.8	20.8		
6	Fwd.Only	0.3/2.7	Fwd.Only	12.871		0.000	1.287	16.00	0.0713	0.2538	28.1	28.1		
7	Fwd.Only	0.9/2.7	Fwd.Only	7.723		0.000	1.931	16.00	0.0871	0.3802	17.6	17.6		
8	15/3	0.3/0.9	0.3/0.9	9.010		9.010	2.252	19.20	0.0832	0.5323	15.6	18.8		
9	15/3	0.9/2.7	0.9/2.7	7.723		7.723	1.931	19.20	0.0864	0.3595	24.0	28.8		
10	45/9	0.3/0.9	0.3/0.9	9.439		9.439	2.360	19.20	0.0876	0.4652	18.8	22.6		
11	45/9	0.9/2.7	0.9/2.7	7.723		7.723	1.931	19.20	0.1011	0.3807	26.6	31.9		
28	45/9	0.9/2.7	0.9/2.7	7.293		7.293	1.823	19.20	0.0891	0.3595	24.8	29.8		
29	120/36	0.3/0.9	0.6/0.6	10.726		5.148	2.681	24.00	0.1502	0.7920	19.0	24.7		
34	90/24	0.3/2.7	0.6/0.6	17.161		3.003	1.716	24.00	0.1290	0.5069	25.4	32.2		
12	Fwd.Only	0.1/0.9	Fwd.Only	27.029		0.000	2.703	8.00	0.0719	0.2661	27.0	27.0		
13	Fwd.Only	0.3/0.9	Fwd.Only	10.726		0.000	2.681	8.00	0.0728	0.2639	27.6	27.6		
14	Fwd.Only	0.3/2.7	Fwd.Only	21.880		0.000	2.188	8.00	0.0711	0.2154	33.0	33.0		
15	Fwd.Only	0.9/2.7	Fwd.Only	8.795		0.000	2.199	8.00	0.0692	0.2164	32.0	32.0		
16	15/3	0.3/0.9	0.3/0.9	14.158		14.158	3.539	9.67	0.0838	0.4213	19.9	23.9		
17	15/3	0.9/2.7	0.9/2.7	11.584		11.584	2.896	9.67	0.0878	0.3447	25.5	30.6		
18	45/9	0.3/0.9	0.3/0.9	14.158		14.158	3.539	9.67	0.0846	0.4213	20.1	24.1		
19	45/9	0.9/2.7	0.9/2.7	11.584		11.584	2.896	9.67	0.0859	0.3447	24.9	29.9		
30	120/36	0.3/0.9	0.6/0.6	13.729		2.145	3.432	16.00	0.0895	0.6759	13.1	17.0		
33	90/24	0.3/2.7	0.6/0.6	27.887		2.145	2.789	16.00	0.1040	0.5492	18.9	24.0		
20	Fwd.Only	0.1/0.9	Fwd.Only	36.467		0.000	3.647	5.33	0.0394	0.2392	16.5	16.5		
21	Fwd.Only	0.3/0.9	Fwd.Only	15.016		0.000	3.754	5.33	0.0361	0.2463	14.7	14.7		
22	Fwd.Only	0.3/2.7	Fwd.Only	31.319		0.000	3.132	5.33	0.0394	0.2055	19.2	19.2		
23	Fwd.Only	0.9/2.7	Fwd.Only	13.729		0.000	3.432	5.33	0.0378	0.2392	15.8	15.6		
24	15/3	0.3/0.9	0.3/0.9	20.593		20.593	5.148	6.67	0.0432	0.4226	10.2	12.3		
25	15/3	0.9/2.7	0.9/2.7	17.161		17.161	4.290	6.67	0.0434	0.3522	12.3	14.8		
26	45/9	0.3/0.9	0.3/0.9	20.593		20.593	5.148	6.67	0.0493	0.4226	11.7	14.0		
27	45/9	0.9/2.7	0.9/2.7	21.182		21.182	5.296	6.67	0.0524	0.4352	12.0	14.4		
31	120/36	0.3/0.9	0.6/0.6	18.448		1.716	4.612	8.00	0.0453	0.4541	10.0	13.0		
35	90/24	0.3/2.7	0.6/0.6	38.613		0.429	3.861	8.00	0.0581	0.3802	15.3	19.4		

From Table VI it is evident that best plating efficiency is obtained in the direct current mode without pulsing, Specimens 1, 2, and 3. For these samples, the peak and average current densities are the same. Highest efficiencies were found in the deposits produced at 1.1 to 2.2 A/dm<sup>2</sup> (10-20 ASF). It might be possible to get similar performance at 3.3 A/dm<sup>2</sup> if higher electrolyte agitation were used. The cathode tube section was rotated in the electrolyte at about seven rpm, but much higher peripheral velocities should be possible with high speed drive motors. Less efficiency was obtained with Specimen 32, and this was the only sample deposited using a pulse duty cycle greater than fifty percent (0.3 msec "on" time and 0.1 msec "off" time for a duty cycle of 75 percent).

It was observed that nearly all specimens of each current density category of Table VI showed better plating efficiency when no use of periodic current reversal was made, as would be expected. The main reason for using periodic current reversal was to determine if visual quality of the deposits might be improved. Figure 4 is an illustration of the platinum study samples with the low numbers to the rear and the high numbers to the front.

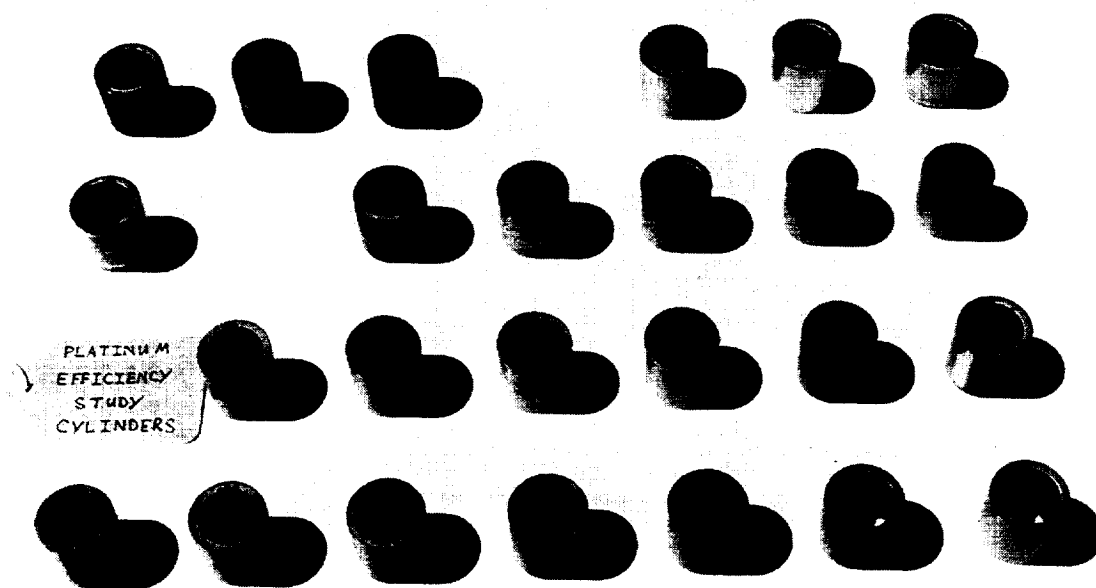


Figure 4. Sel-Rex Platanex III Platinum Efficiency Test Samples.

Of the direct current plated samples, Specimen 2 had the best appearance with respect to color and smoothness. Specimen 1 was unexpectedly rough - perhaps due to a newly prepared and carbon treated bath which may have had some carbon fines that were not

retained by the filter paper. Specimen 3 was rough, but this was likely due to the high current density used. As shown in Figure 5, current efficiency peaks at just under 40 percent for the lower current densities.

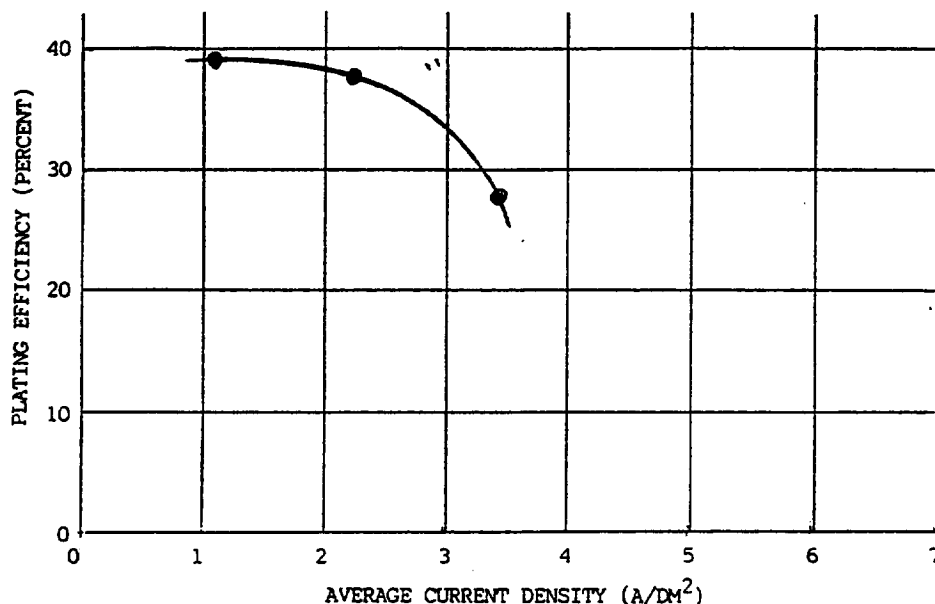


Figure 5. Platanex III Bath Plating Efficiencies Using Conventional Direct Current.

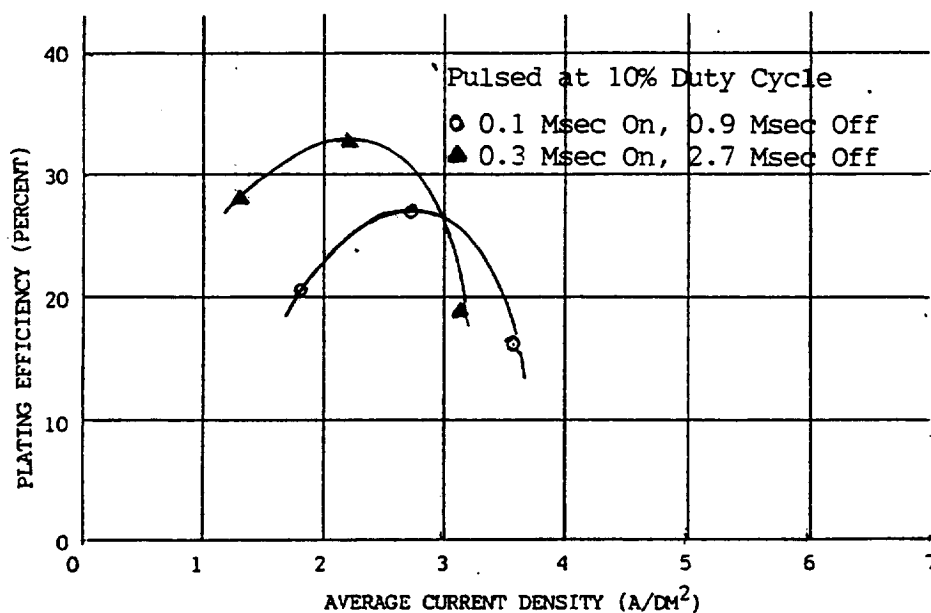


Figure 6. Platanex III Bath Plating Efficiencies Using Pulsed Current With a 10 Percent Duty Cycle.

Plating efficiencies for Platanex III deposits pulse current deposited with a 10 percent duty cycle are plotted in Figure 6. It

is noted that efficiency improves with longer "on" and "off" time (lower frequency cycles). Figure 7 indicates that increasing the duty cycle to 25 percent for comparable "on" and "off" times does not make any significant change in plating efficiencies. This is significant in that it indicates that "negative" duty cycles - that is, duty cycles less than 50 percent - may be limited to a maximum efficiency because of the high peak current densities involved. Most investigators are of an opinion that platinum must be in specific complexed forms to produce sound deposits. High peak current densities present in low duty cycle pulse plating likely result in rapid reduction of these complexes and there is a time factor involved in migration of replenishment platinum complexes into the catholyte region. These complexes probably have a low mass transfer rate due to their large diameters.

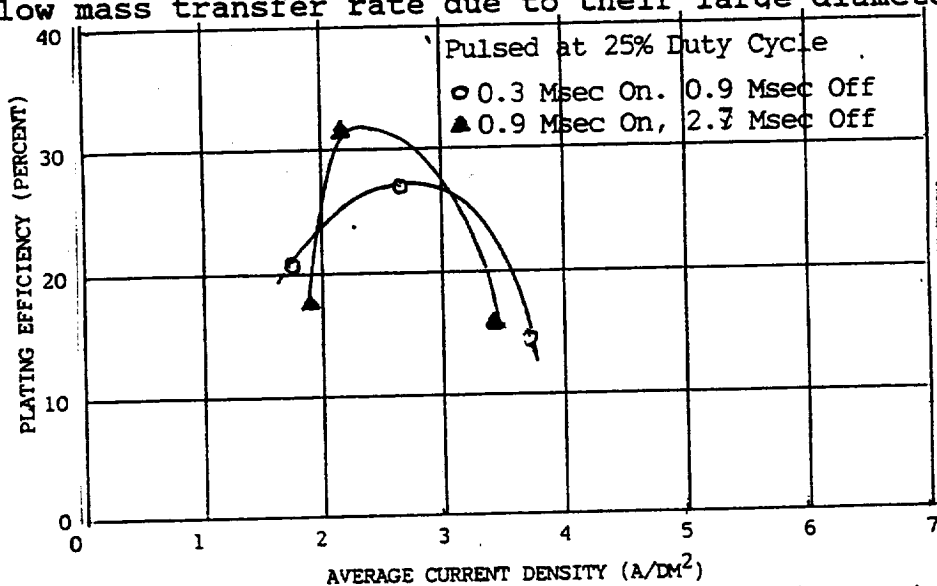


Figure 7. Platanex III Bath Plating Efficiencies Using Pulsed Current With a 25 Percent Duty Cycle.

Figures 8 and 9 compare the platinum plating efficiencies from the Platanex III bath when pulsed, periodic reverse (PR) current is used. Since the platinum deposit acts as an inert anode during the reversal cycle, the net effect of the reversal stage is basically an extension of the "off" time from the last pulse of the "forward" plating direction. This extra time allows chemical equilibrium to be restored to offset problems from high peak current densities. Increasing the PR forward and reverse time by a factor of three did not show any significant changes in plating efficiencies, Figure 9.

Platanex III specimens plated at the higher apparent current densities shown in Table V had much darker appearances and were found to plate at significantly lower current efficiencies. Except for Specimen 10, which was unaccountably rough surfaced, all of the samples deposited at apparent average current densities



from 1 to 2 A/dm<sup>2</sup> were of good physical appearance. As would be expected, all samples produced with periodic current reversal as part of the plating cycle had lower plating efficiencies.

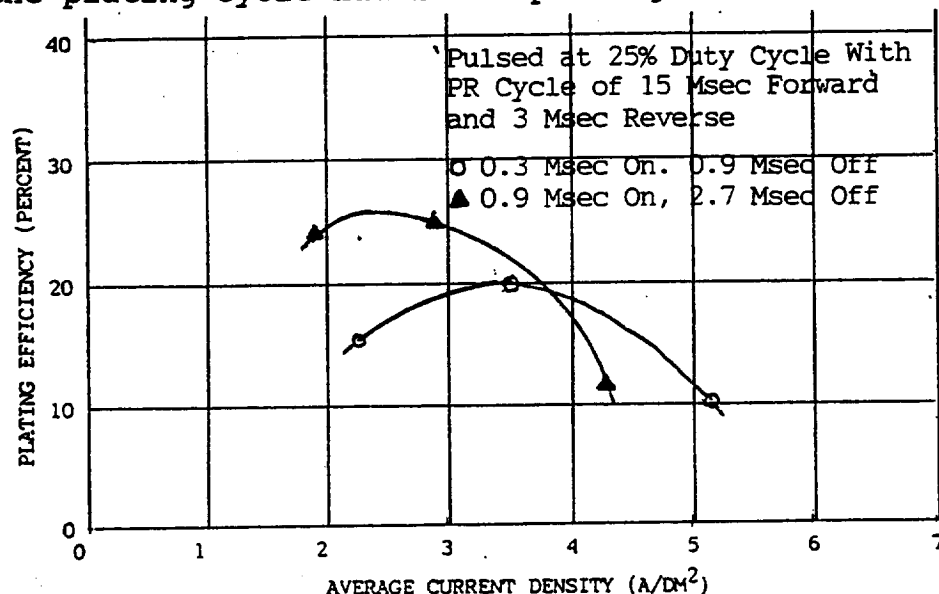


Figure 8. Platanex III Bath Plating Efficiencies Using Pulsed Current With Periodic Reversed Current at Cycles of 15 Msec Forward and 3 Msec Reverse.

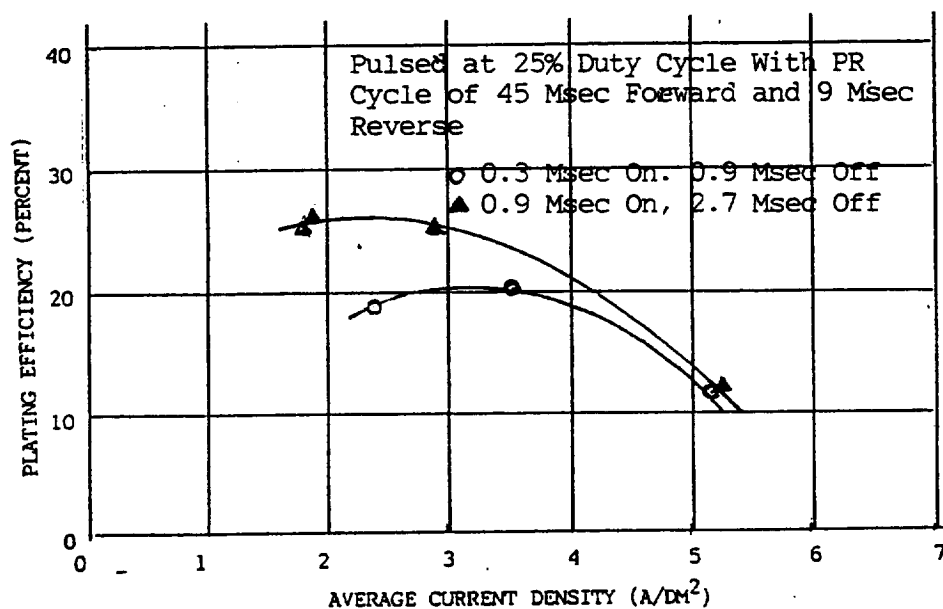


Figure 9. Platanex III Bath Plating Efficiencies Using Pulsed Current With Periodic Reversed Current At Cycles of 45 Msec Forward and 9 Msec Reverse.

Although the copper cylinder specimens were plated with an 0.002 inch nickel layer and a gold strike to minimize corrosive attack

on the copper substrate, leakage of plating solution into the interior sometimes occurred which corroded the electrical contact from the rotating shaft. Teflon O-rings were used to seal these leaks. A further step to reduce corrosion was taken by striking the gold plated surfaces with a near-neutral pH chloroplatinic acid bath. Weighings before platinum plating from the Platanex III bath were made with the neutral platinum strike applied. As platings were made, weighings for platinum plated were accumulated and appropriate platinum metal replacements made to the bath.

Analysis of platinum electrolytes for platinum metal content was of greater concern than expected. Comparisons of test results from several laboratories using various analytical methods showed inconsistencies. It was found necessary to send samples to vendors more experienced in analyzing platinum group metals on a routine basis and usually free of charge. The only disadvantage of this was the time required to send samples to the supplier's laboratories. However, if analyses of the same bath sample can be made by the supplier and a more local analytical laboratory, a factor may be determined to permit bath control based on the local laboratory results.

#### **Platinum Thickness Studies**

The purpose of this study was to determine the maximum thickness of crack-free platinum that could be deposited from the Sel-Rex Platanex III bath based on the more favorable plating conditions identified in the prior plating efficiency study. In the first part of this study, platinum was deposited from only the Platanex III bath. A summary of the plating parameters, deposit physical measurements, and appearance is found in Table VI. The initial sample plated was from an electrolyte with no wetting agent present. The next sample was started without wetting agent, but after two hours of plating, it was noted that the shiny surface contained numerous pits - most likely from hydrogen. This prompted addition of an extremely small amount of sodium laurel sulfate, a widely accepted wetting agent for acid based electrolytes.

Test specimens were created by cutting 0.130 inch wall thickness copper tubing, of 1 inch diameter, into 1 inch lengths. Each of these samples was plated with 0.001 inch of nickel and struck with several microns of gold. The average area of each specimen for plating purposes was 3.17 in<sup>2</sup>. Anodes were platinum clad titanium mesh. Test cylinders were cleaned with isopropyl alcohol and scrubbed with Alconox detergent solution. Activation of the cylinders was performed by dipping in concentrated hydrochloric acid for a few seconds, rinsing in deionized water, and immersing in the platinum bath with voltage applied. The wetting agent, when present, was at a concentration of 0.012 g/l. The

TABLE VI - PLATINUM THICKNESS STUDY RESULTS

SEL-REX PLATANEX III PLATINUM PLATING THICKNESS STUDIES											
SPECIMEN NUMBER	DIRECTION	FORWARD		REVERSE		PEAK FORWARD CUR. DENS. (Amp/Dm <sup>2</sup> )	PEAK REVERSE CUR. DENS. (Amp/Dm <sup>2</sup> )	PLATING TIME (Hours)	CALCULATED AVERAGE CUR. DENS. (Amp/Dm <sup>2</sup> )	DUTY CYCLE (%)	DEPOSIT THICKNESS (In)
		PULSE ON/OFF (Milli sec)	PULSE ON/OFF (Milli sec)	PULSE ON/OFF (Milli sec)	PULSE ON/OFF (Milli sec)						
THICKNESS STUDY - PART I											
1	FWD. ONLY	0.1/0.9	NONE	27.029	0.000	6.00	2.703	10	0.00263	Rough and nodular.	
2	FWD. ONLY	0.1/0.9	NONE	27.458	0.000	4.00	2.746	10	0.00187	Pitted and nodular.	
3	FWD. ONLY	0.1/0.9	NONE	27.458	0.000	4.00	2.746	10	0.00163	Nodular.	
4	FWD. ONLY	DC ONLY	NONE	2.145	0.000	1.60	2.145	100	0.00063	Pitted and nodular.	
5	FWD. ONLY	DC ONLY	NONE	1.233	0.000	5.20	1.233	100	0.00126	Rough.	
6	15.0/3.0	0.9/2.7	0.9/2.7	12.013	12.013	3.50	3.003	25/25	0.00152	Cracked bot. edge.	
THICKNESS STUDY - PART II											
1	45.0/9.0	0.9/2.7	0.9/2.7	6.864	6.864	1.00	1.716	25/25	0.00028	Good except ends.	
2	45.0/9.0	0.9/2.7	0.9/2.7	7.293	7.293	1.87	1.823	25/25	0.00049	Good; ends cracked.	
3	45.0/9.0	0.9/2.7	0.9/2.7	7.293	5.577	1.50	1.823	25/25	0.00044	Good; ends cracked.	
4	FWD. ONLY	0.9/2.7	NONE	5.148	0.000	1.50	1.287	25	0.00046	Good; ends cracked.	
5	36.0/6.0	0.9/2.7	3.0/3.0	6.006	0.977	1.00	1.502	25/50	0.00036	Good; ends cracked.	
USE OF PLATINUM AP BATH:											
SPECIMEN NUMBER	REMARKS										
1	Preplated with 0.0153 g of Pt from AP Bath prior to Platanex III.										
2	Preplated with 0.0198 g of Pt from AP Bath prior to Platanex III.										
3	Above samples had edge undercutting from anodic action in PR reverse cycle.										
4	Preplated with Pt from AP Bath prior to Platanex III. Reverse in Platanex III delayed for 20 min.										
5	Undercutting still noted on corners.										
6	Preplated with Pt from AP Bath prior to Platanex III. Used forward pulse current only. Appearance improved, but localized exposure of copper noted on top edge.										
7	Preplated with Pt from AP Bath prior to Platanex III for longer time to reduce corrosive attack on edges where Teflon seals applied. Cracking at corners of edges still found.										
		</									

wetting agent created a thin foam blanket on the electrolyte resulting in the bath temperature increasing. Use of a waterjacket container around the plating solution beaker helped control this.

As noted in Table VI, the Part I specimens were unsatisfactory as a result of roughness and cracking. Reasons for this performance were believed to be:

- (1) the high peak current densities which led to stress build-up in high current density areas such as edges,
- (2) corrosion of the substrate due to much longer exposure times in the electrolyte having a pH of about 1.5, and
- (3) inadequate sealing of specimen edges.

Much of the roughness must be attributed to corrosive attack by the electrolyte on the substrate whereby pits and salts were produced. Efforts to overcome these problems were performed in the Part II study of Table VI. Improved Teflon fixturing was made, larger Teflon O-rings were used, wetting agent was added to the plating bath, and a near neutral Platinum AP bath (based on hexachloroplatinic acid) was used as a preplate to protect the substrate. The substrate was susceptible to chemical attack because the combined nickel and gold protective coatings were too thin (and thus porous). It could be argued that thicker strike coatings would overcome this problem; however, it must be remembered that such strikes will produce alloys having low melting eutectics at elevated temperature - thus defeating the coating primary function.

Part II studies, Table VI, disclosed that these new measures resulted in smooth coatings, but cracking from high stress still occurred at the edges of the cylinders. The pulse duty cycle had been changed to assure lower peak current densities, but this did not solve the cracking problem. At this point it was determined that the Platanex III bath should not be used for thick initial coatings on sensitive substrates. However, use of the bath for rapid build-up of platinum over other platinum sealing coatings was not dismissed. Platinum plating was shifted to the AP Bath (hexachloroplatinate complexed by aminophosphates). As will be shown later, this bath proved satisfactory in thick build-up on many substrates.

#### **Rhodium - State of the Art**

Raub [14] describes rhodium electrolytes as based on simple salts of rhodium or on special rhodium complexes. He notes that most rhodium electrolytes have been formulated to produce deposits of only 1  $\mu\text{m}$  or less. The deposits have a high concentration of non-metallic impurities (e.g., up to 1000 ppm H and/or O), which

causes high hardnesses and internal stresses, which often result in cracks. Thin rhodium layers are highly porous. This, coupled with the high electrochemical nobility of the metal, limits its use as a corrosion protection layer. Nickel is not recommended for a base coating between substrates and rhodium.

Complexed rhodium salts listed in the literature are based on sulfate, phosphate, sulfate-phosphate, sulfamate, fluoborate, chloride, nitrate, and perchlorate solutions. A typical production bath consists of rhodium sulfate in a sulfuric acid solution. Raub notes that certain sulfur containing compounds may be used as additives to control stress and produce crack-free layers to thicknesses of about 10  $\mu\text{m}$ . He also states that the temperature of such baths is about 50°C, and the current density ranges from 1 to 10 A/dm<sup>2</sup>. The current efficiency is reportedly 80 percent. Insoluble anodes are normally used. Raub suggests rhodium electrolytes for engineering applications as shown in Table VII.

TABLE VII - LOW-STRESS RHODIUM ELECTROLYTES FOR ENGINEERING USE

Solution	Selenic acid process	Magnesium sulfamate process
Rhodium (sulfate complex)	10 g/L (1.3 oz/gal)	2-10 g/L (0.3-1.3 oz/gal)
Sulfuric acid (concentrated)	15-200 mL/L (2-26 fluid oz/gal)	5-50 mL/L (0.7-7 fluid oz/gal)
Selenic acid	0.1-1.0 g/L (0.01-0.1 oz/gal)	...
Magnesium sulfamate	...	10-100 g/L (1.3-13 oz/gal)
Magnesium sulfate	...	0-50 g/L (0-7 oz/gal)
Current density	1-2 A/dm <sup>2</sup> (10-20 A/ft <sup>2</sup> )	0.4-2 A/dm <sup>2</sup> (4-22 A/ft <sup>2</sup> )
Temperature	50-75 °C (120-165 °F)	20-50 °C (68-120 °F)

According to Safranek [15], rhodium deposits show high tensile stress values. Tensile stress values from the sulfate type baths have been reported as ranging from about 50 to 100 kg/mm<sup>2</sup> (70 to 140 ksi). Increasing sulfuric acid concentration, current density, and/or temperature reduces stress. Safranek noted that the rough and dark deposits from sulfate baths were usually of lower stress than those that were bright and smooth. Increasing the sulfuric acid concentration to about 100 ml/l promotes a smooth gray deposit with a progressive reduction in stress to a constant value with no further reduction with higher acid contents. Value of internal stress in sulfate rhodium deposits from a bath with 5 g/l rhodium and 20 ml/l of sulfuric acid at 50°C and 2 A/dm<sup>2</sup> is reportedly about 56 kg/mm<sup>2</sup> (80 ksi). Deposits are usually not cracked at thicknesses to 5  $\mu\text{m}$ . Cracking may occur in thicker deposits, but flaking will not occur if proper steps are taken to obtain good adhesion. The substrate does not appear to significantly affect stress in rhodium deposits; however, a stressed substrate will lead to increased number of cracks in the deposit.

According to Hansel [16], crack-free deposits from the sulfate bath are best obtained at a bath temperature of about 50°C, a rhodium concentration of at least 5 g/l, and a sulfuric acid concentration of 15 to 30 g/l. Reid [17] claimed cracks in rhodium

could be eliminated at thicknesses to 12.5  $\mu\text{m}$  by adding 20 g/l of aluminum as aluminum sulfate to a bath containing 10 g/l rhodium and 50 ml/l sulfuric acid; however, this additive in excess of 5 g/l tended to produce unacceptable deposit finishes. Magnesium or aluminum sulfate additions of 6 g/l yielded crack-free rhodium deposits to 12.5  $\mu\text{m}$  when the bath contained 6 g/l rhodium

Kadaner [18] reported that internal stress can be reduced by lowering the concentration of sulfuric acid to 16 g/l with rhodium at 2.7 g/l and heating the deposits in vacuum to 400 to 500°C for 20 to 30 minutes. Heating decreased the hydrogen content by about 75 percent. Reid [19] claimed crack-free rhodium deposits of 12.5 to 25.4  $\mu\text{m}$  thickness using 0.1 to 1.0 g/l selenic acid as an additive to sulfate solutions containing a minimum of 10 g/l rhodium and 15 to 200 ml/l sulfuric acid at 50 to 75°C and 1 to 2 amp/sq dm. Reid [20] further noted that stress with selenic acid additions is slightly higher than that without the additions for deposits up to about 1  $\mu\text{m}$  thickness when stress relief attributed to microcracking becomes apparent; it then decreases steadily to very low values as deposit thickness increases. Deposits obtained from rhodium baths with selenic acid contain microcracks which can be developed by etching; however, cracks formed initially tend to heal with increasing thickness until a deposit is formed which may be regarded as crack-free from a corrosion protection standpoint.

A summary of relative stress levels developed in rhodium deposits from electrolytes containing various addition agents is found in Table VIII.

TABLE VIII - RELATIVE STRESS OF RHODIUM DEPOSITS FROM A SULFATE ELECTROLYTE WITH VARIOUS ADDITION AGENTS (a)

Rhodium, g/l	Sulfuric Acid, ml/l	Selenic Acid, ml/l	Magnesium, g/l	Copper, g/l	Deflection of Cathode, mm			
					1.3 $\mu\text{m}$	2.5 $\mu\text{m}$	3.8 $\mu\text{m}$	5.0 $\mu\text{m}$
10	nil	nil	nil	nil	2.79	6.65	10.5	14.0
10	nil	1.0	nil	nil	4.23	5.85	6.29	5.92
10	50	1.0	nil	nil	3.63	2.54	2.01	1.69
10	50	1.0	nil	1.0	2.78	1.69	0.84	0.29
5	50	nil	6	nil	5.55	11.50	15.2	(b)
5	50	nil	6	1.0	7.75	13.65	15.95	16.70

<sup>(a)</sup> Deposits at 1 amp/sq dm and 50 C.

<sup>(b)</sup> An absolute stress of 81 kg/sq mm was obtained for deposits of up to 12.5  $\mu\text{m}$

### Rhodium Plating Efficiency Studies

The rhodium electrolyte was prepared from commercially available rhodium sulfate concentrate containing 1 gram of rhodium per 200

ml of stock solution. Starting with 500 ml of deionized water, a sulfuric acid addition of about 26 ml was made. About 10 grams of rhodium was added from the concentrate. This solution was diluted with deionized water to a total volume of 1 liter. 90 ml was retained for analytical reference purposes. Bath temperature ranged from 45 to 46°C. Bath temperature and solution agitation were maintained on a programmed hotplate-stirrer. Stress reducing additives were not used in the efficiency studies other than any that might have been present in the proprietary rhodium sulfate concentrate purchased from Technic, Inc. under the trade name of Rhodium Sulfate TP.

The specimens used as substrates in this study have previously been described under platinum efficiency studies. These samples were rotated on a shaft with a variable speed drive with current passed by means of a mercury well. This bath is very acidic, and it was necessary to nickel and gold plate the copper substrate to prevent corrosive attack which might contaminate the expensive rhodium bath. This also accounts for the use of a small volume bath which could be economically replaced in event of contamination. A Yokogawa calibrated primary standard quality ammeter was used to record apparent current densities during pulse plating. A record of plating parameters, specimen weight changes resulting from rhodium deposition, and calculated plating efficiencies for the samples from the electrolyte containing 10 g/l rhodium and 25 ml/l sulfuric acid will be found in Table IX.

Samples 1 through 3 were plated with conventional direct current at different current densities within the range recommended for rhodium sulfate baths. Current efficiencies were calculated from actual deposit weights obtained as a percent of the theoretical weight expected for the ampere-hours of current used. Figure 10 shows that current efficiencies are high (over 90 percent) for each current density examined. Figure 10 also shows that use of

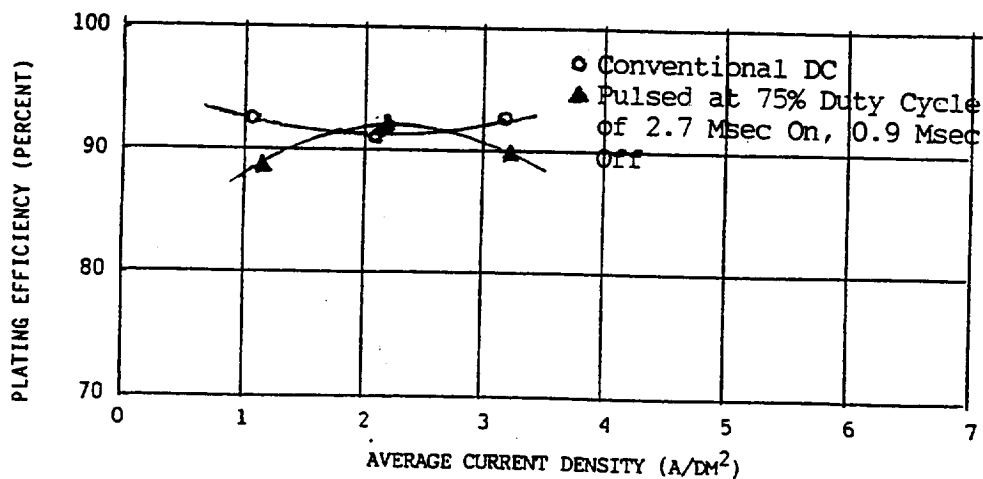


Figure 10. Acid Rhodium Sulfate Bath Plating Efficiencies Using Conventional Direct Current and 75 Percent Pulse Duty Cycles.

TABLE IX - RHODIUM PLATING EFFICIENCY STUDY (HIGH METAL, LOW ACID BATH)

ACID RHODIUM SULFATE PLATING EFFICIENCY STUDIES - RH (10 G/L), H2BO4 (25 ML/L)										TOTAL			
SPECIMEN NUMBER	DIRECTION	FORWARD		REVERSE		PEAK		CALCULATED		PLATING TIME (minutes)	DEPOSIT WEIGHT (Grams)	WEIGHT AT 100% EFFICIENCY (Grams)	TOTAL CYCLE
		PULSE ON/OFF (msec)	PULSE ON/OFF (msec)	PULSE ON/OFF (msec)	PULSE ON/OFF (msec)	CUR. DENS. (Amp/Dm <sup>2</sup> )	REVERSE CUR. DENS. (Amp/Dm <sup>2</sup> )	AVERAGE CUR. DENS. (Amp/Dm <sup>2</sup> )	TIME (minutes)				PLATING EFF. (%)
1	Fwd. Only	DC Only	DC Only	Fwd. Only	Fwd. Only	1.070	0.000	1.070	16.00	0.0685	0.0685	0.0741	92.5
2	Fwd. Only	DC Only	DC Only	Fwd. Only	Fwd. Only	2.140	0.000	2.140	8.00	0.0674	0.0674	0.0741	91.0
3	Fwd. Only	DC Only	DC Only	Fwd. Only	Fwd. Only	3.235	0.000	3.235	6.00	0.0769	0.0769	0.0831	92.6
4	Fwd. Only	0.1/0.9	0.1/0.9	Fwd. Only	Fwd. Only	10.700	0.000	1.070	16.00	0.0536	0.0536	0.0741	72.3
5	Fwd. Only	0.1/0.9	0.1/0.9	Fwd. Only	Fwd. Only	10.700	0.000	1.070	16.00	0.0491	0.0491	0.0741	66.3
7	Fwd. Only	0.3/0.9	0.3/0.9	Fwd. Only	Fwd. Only	4.696	0.000	1.174	16.00	0.0776	0.0776	0.0813	95.5
8	Fwd. Only	0.3/2.7	0.3/2.7	Fwd. Only	Fwd. Only	11.740	0.000	1.174	17.00	0.0771	0.0771	0.0863	89.4
9	Fwd. Only	0.9/2.7	0.9/2.7	Fwd. Only	Fwd. Only	6.904	0.000	1.726	16.00	0.0848	0.0848	0.1194	71.0
14	15/3	0.3/0.9	0.3/0.9	0.3/0.9	0.3/0.9	8.876	0.000	2.219	16.00	0.0672	0.1536	0.1536	52.6
15	15/3	0.3/0.9	0.3/0.9	0.3/0.9	0.3/0.9	10.356	10.356	2.589	19.20	0.0685	0.2150	0.2150	38.3
16	15/3	0.9/2.7	0.9/2.7	0.9/2.7	0.9/2.7	8.383	8.383	1.726	19.20	0.0800	0.1433	0.1433	55.8
19	45/9	0.9/2.7	0.9/2.7	0.9/2.7	0.9/2.7	8.383	8.383	2.219	19.20	0.0807	0.1843	0.1843	43.8
20	45/9	0.3/0.9	0.3/0.9	0.3/0.9	0.3/0.9	10.356	10.356	2.589	19.20	0.0798	0.2150	0.2150	44.5
27	Fwd. Only	0.9/2.7	0.9/2.7	Fwd. Only	Fwd. Only	6.904	0.000	1.726	16.00	0.0786	0.1194	0.1194	65.8
6	Fwd. Only	0.1/0.9	0.1/0.9	Fwd. Only	Fwd. Only	24.164	0.000	2.416	8.00	0.0491	0.0836	0.0836	58.7
10	Fwd. Only	0.1/0.9	0.1/0.9	Fwd. Only	Fwd. Only	33.533	0.000	3.353	8.00	0.0675	0.1160	0.1160	58.2
11	Fwd. Only	0.3/0.9	0.3/0.9	Fwd. Only	Fwd. Only	12.822	0.000	3.205	8.00	0.0725	0.1109	0.1109	65.4
12	Fwd. Only	0.3/2.7	0.3/2.7	Fwd. Only	Fwd. Only	27.123	0.000	2.712	8.00	0.0688	0.0938	0.0938	73.3
13	Fwd. Only	0.9/2.7	0.9/2.7	Fwd. Only	Fwd. Only	10.356	0.000	2.589	8.00	0.0678	0.0896	0.0896	75.7
17	15/3	0.3/0.9	0.3/0.9	0.3/0.9	0.3/0.9	16.767	16.767	4.192	9.67	0.0780	0.1753	0.1753	53.4
18	15/3	0.9/2.7	0.9/2.7	0.9/2.7	0.9/2.7	13.808	13.808	3.452	9.67	0.0807	0.1444	0.1444	67.1
21	45/9	0.3/0.9	0.3/0.9	0.3/0.9	0.3/0.9	16.767	16.767	4.192	9.67	0.0719	0.1753	0.1753	49.2
22	45/9	0.9/2.7	0.9/2.7	0.9/2.7	0.9/2.7	14.794	14.794	3.699	9.67	0.0808	0.1547	0.1547	62.7
31	Fwd. Only	0.3/0.9	0.3/0.9	Fwd. Only	Fwd. Only	16.767	0.000	4.192	6.00	0.0740	0.1088	0.1088	68.0
32	Fwd. Only	0.3/2.7	0.3/2.7	Fwd. Only	Fwd. Only	35.999	0.000	3.600	6.00	0.0767	0.1195	0.1195	64.2
23	15/3	0.9/2.7	0.9/2.7	0.9/2.7	0.9/2.7	23.671	23.671	5.918	7.20	0.0747	0.1843	0.1843	48.6
24	45/9	0.9/2.7	0.9/2.7	0.9/2.7	0.9/2.7	20.712	20.712	5.178	7.20	0.0834	0.1612	0.1612	62.1
25	45/9	0.3/0.9	0.3/0.9	0.3/0.9	0.3/0.9	23.177	23.177	5.794	7.20	0.0724	0.1804	0.1804	48.1
26	15/3	0.3/0.9	0.3/0.9	0.3/0.9	0.3/0.9	23.177	23.177	5.794	7.20	0.0774	0.1804	0.1804	51.5
28	Fwd. Only	2.7/0.9	2.7/0.9	Fwd. Only	Fwd. Only	2.466	Fwd. Only	1.208	16.00	0.0744	0.0836	0.0836	89.0
29	Fwd. Only	2.7/0.9	2.7/0.9	Fwd. Only	Fwd. Only	3.945	Fwd. Only	2.268	8.00	0.0717	0.0785	0.0785	91.4
30	Fwd. Only	2.7/0.9	2.7/0.9	Fwd. Only	Fwd. Only	5.425	Fwd. Only	3.255	8.00	0.0759	0.0845	0.0845	89.9



pulsed current at high duty cycles (over 50 percent) contributes to high plating efficiencies. However, quality of the deposit is of like concern, so a wide variety of pulsing conditions were investigated.

Figure 11 illustrates effects of pulse duration on plating efficiencies. For a pulse duty cycle of 10 percent, longer pulse durations lead to better efficiencies than those of short duration.

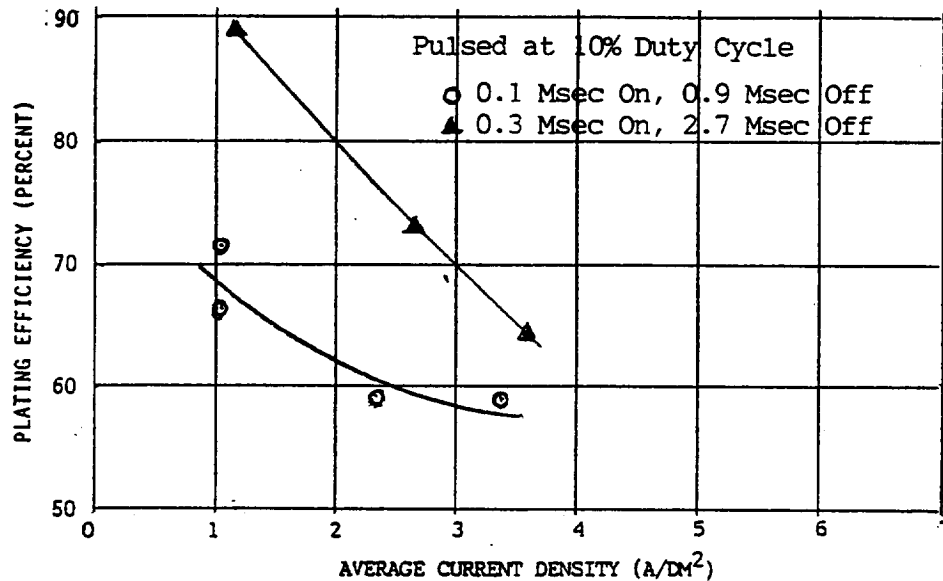


Figure 11. Acid Rhodium Sulfate Bath Plating Efficiencies Using Pulsed Current With a 10 Percent Duty Cycle.

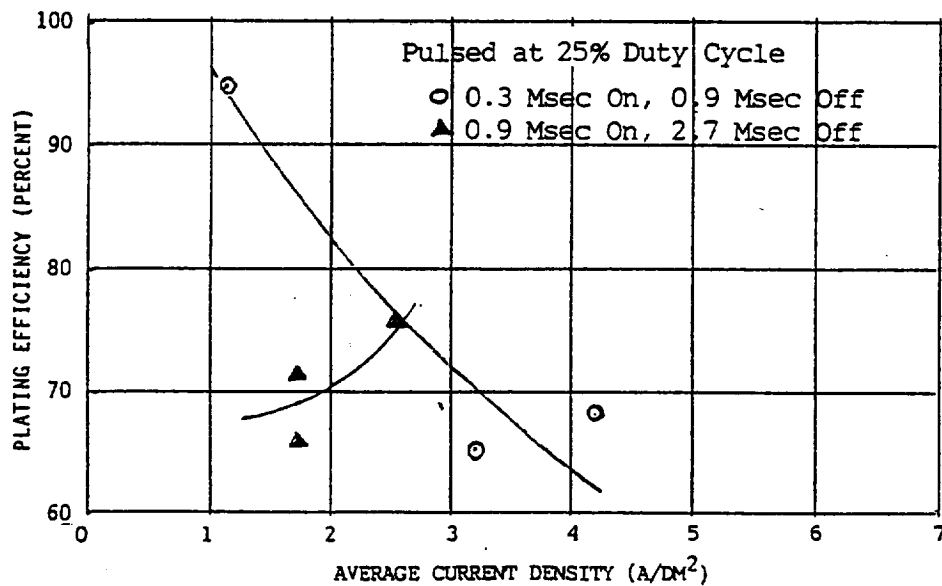


Figure 12. Acid Rhodium Sulfate Bath Plating Efficiencies Using Pulsed Current With a 25 Percent Duty Cycle.

Increasing the pulse duty cycle to 30 percent for forward direction pulse plating resulted in improved plating efficiencies as shown in Figure 12. Note that Specimen No. 9 indicated an unusually high efficiency of almost 100 percent. A repetition of this sample was made which disclosed 92 percent efficiency, Specimen No. 27. At this higher duty cycle, the pulse duration does not appear to significantly affect plating efficiency.

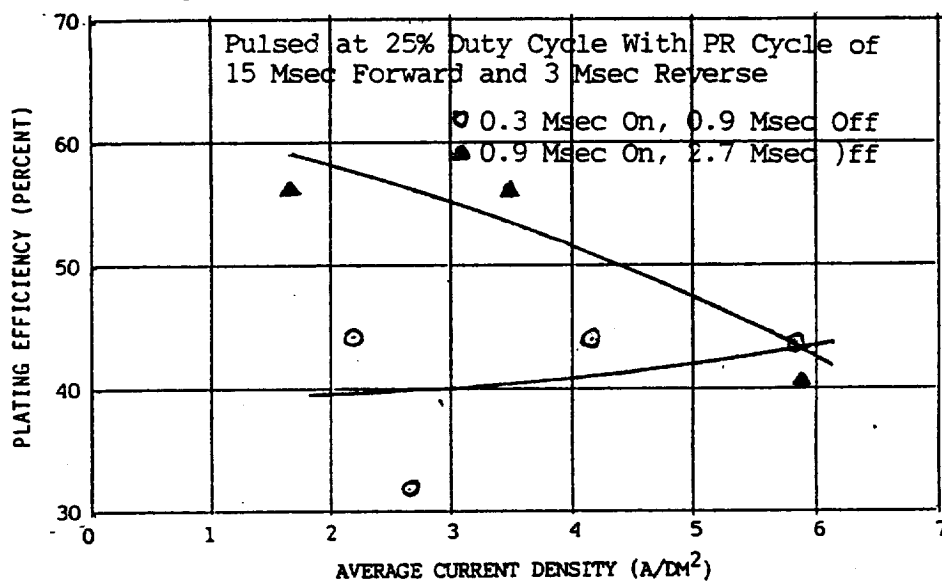


Figure 13. Normal Acid Rhodium Sulfate Bath Plating Efficiencies Using Pulsed Current With Periodic Reversed Current at Cycles of 15 Msec Forward and 3 Msec Reverse.

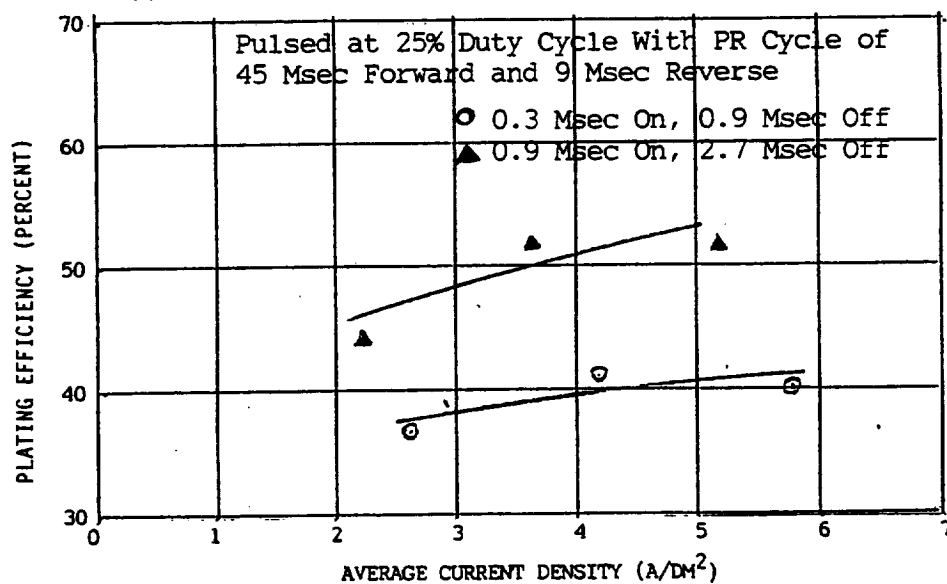


Figure 14. Normal Acid Rhodium Sulfate Bath Plating Efficiencies Using Pulsed Current With Periodic Reversed Current at Cycles of 45 Msec Forward and 9 Msec Reverse.

Figures 13 and 14 are graphic presentations of data from rhodium plated specimens in which the current was pulsed with periodic current reversal. Figure 13 represents shorter PR cycle durations, while Figure 14 represents longer PR cycle durations. Inadvertent omission of current in the reversal cycle of Specimen No. 14 led to a repetition of this specimen (Specimen 15) in Figure 13. Generally, the shorter PR cycle and longer pulse cycle durations resulted in better plating efficiencies, but the efficiencies with conventional DC and pulse duty cycles above 50 percent were superior.

Figure 15 shows the rhodium plating efficiency specimens with the highest numbered samples in the front and the lowest numbered to the rear. Specimen Nos. 4, 8, 15, and 23 exhibited some form of cracking believed due to thin gold strike and hydrogen entrapment at Teflon sealed edges (Specimens 4 and 8) and anodic attack on thin, porous gold during PR anodic cycles (Specimens 15 and 23).

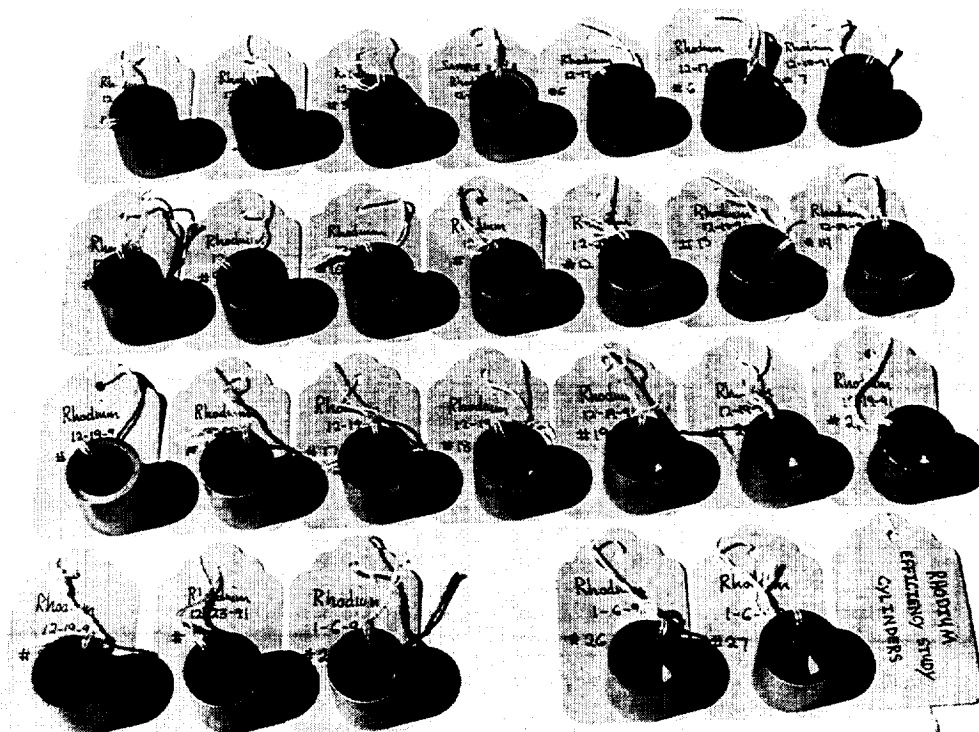


TABLE X - RHODIUM PLATING EFFICIENCY STUDY (NORMAL METAL, VARIED ACID BATHS)

ACID RHODIUM SULFATE PLATING EFFICIENCY STUDIES														
SPECIMEN NUMBER	DIRECTION TIME	FORWARD		REVERSE		PEAK		CALCULATED		PLATING TIME (Minutes)	DEPOSIT WEIGHT (Grams)	WEIGHT AT 100% EFFICIENCY (Grams)	TOTAL CYCLE PLATING EFF. (%)	FORWARD CURRENT PLATING EFF. (%)
		ON/OFF (MilliSec)	PULSE	ON/OFF (MilliSec)	PULSE	CUR. DENS. (Amp/Dm <sup>2</sup> )	CUR. DENS. (Amp/Dm <sup>2</sup> )	CUR. DENS. (Amp/Dm <sup>2</sup> )	CUR. DENS. (Amp/Dm <sup>2</sup> )					
Bath Contained 10 g/l Rhodium and 50 ml/l Sulfuric Acid														
33	Fwd. Only	0.3/2.7	Fwd. Only	14.794		0.000	1.479		1.479	16.00	0.0643	0.1310	49.1	49.1
34	Fwd. Only	0.3/2.7	Fwd. Only	25.643		0.000	2.564		2.564	8.00	0.0682	0.1135	60.1	60.1
35	Fwd. Only	0.3/2.7	Fwd. Only	35.999		0.000	3.600		3.600	6.00	0.0749	0.1195	62.7	62.7
Bath Contained 5 g/l Rhodium and 25 ml/l Sulfuric Acid														
36	Fwd. Only	0.3/2.7	Fwd. Only	14.794		0.000	1.479		1.479	16.00	0.0680	0.1310	51.9	51.9
37	Fwd. Only	0.3/2.7	Fwd. Only	25.643		0.000	2.564		2.564	8.00	0.0549	0.1135	48.4	48.4
38	Fwd. Only	0.3/2.7	Fwd. Only	36.492		0.000	3.649		3.649	6.00	0.0505	0.1212	41.7	41.7
Bath Contained 5 g/l Rhodium and 50 ml/l Sulfuric Acid														
39	Fwd. Only	0.3/2.7	Fwd. Only	14.301		0.000	1.430		1.430	16.00	0.0656	0.1266	51.8	51.8
40	Fwd. Only	0.3/2.7	Fwd. Only	26.136		0.000	2.614		2.614	8.00	0.0457	0.1157	39.5	39.5
41	Fwd. Only	0.3/2.7	Fwd. Only	26.136		0.000	2.614		2.614	8.00	0.0507	0.1157	43.8	43.8
42	Fwd. Only	0.3/2.7	Fwd. Only	36.492		0.000	3.649		3.649	6.00	0.0419	0.1212	34.6	34.6
Bath Contained 5 g/l Rhodium and 75 ml/l Sulfuric Acid														
43	Fwd. Only	0.3/2.7	Fwd. Only	14.794		0.000	1.479		1.479	16.00	0.0586	0.1310	44.7	44.7
44	Fwd. Only	0.3/2.7	Fwd. Only	25.643		0.000	2.564		2.564	8.00	0.0400	0.1135	35.2	35.2
45	Fwd. Only	0.3/2.7	Fwd. Only	35.999		0.000	3.600		3.600	6.00	0.0340	0.1195	28.4	28.4
Bath Contained 5 g/l Rhodium and 100 ml/l Sulfuric Acid														
46	Fwd. Only	0.3/2.7	Fwd. Only	15.287		0.000	1.529		1.529	16.00	0.0568	0.1354	41.9	41.9
47	Fwd. Only	0.3/2.7	Fwd. Only	26.136		0.000	2.614		2.614	8.00	0.0401	0.1157	34.7	34.7
48	Fwd. Only	0.3/2.7	Fwd. Only	35.999		0.000	3.600		3.600	6.00	0.0274	0.1195	22.9	22.9

shown in Figure 16. Lowering the rhodium concentration of the bath from 10 g/l to 5 g/l, while maintaining sulfuric acid at 25 ml/l results in a significant decrease in plating efficiency with increasing current density as illustrated in Figure 17.

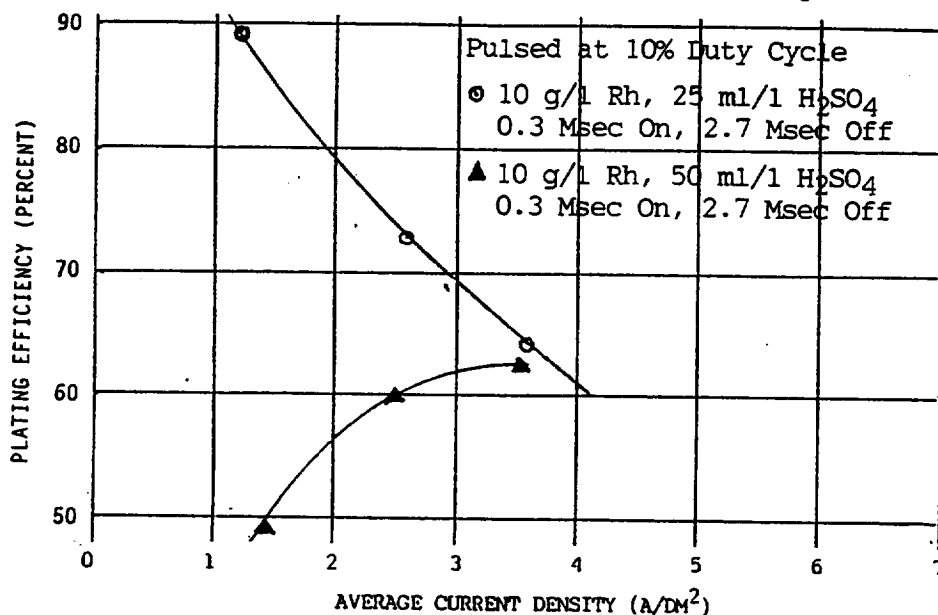


Figure 16. Comparison of Rhodium Plating Efficiencies for Acid Sulfate Baths With 10 g/l Rhodium, 25 and 50 ml/l H<sub>2</sub>SO<sub>4</sub>, and a Pulsed Current Duty Cycle of 10 Percent.

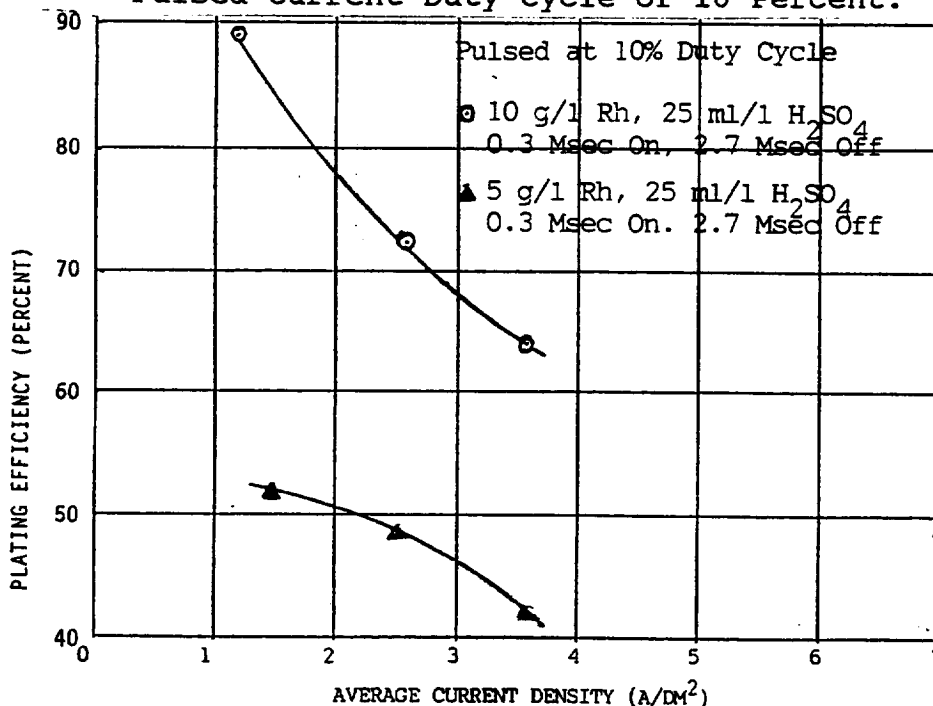


Figure 17. Comparison of Rhodium Plating Efficiencies for Acid Sulfate Baths With 25 ml/l H<sub>2</sub>SO<sub>4</sub>, 5 and 10 g/l Rhodium, and a Pulsed Current Duty Cycle of 10 Percent.

Figure 18 depicts the effect of increasing sulfuric acid content on acid rhodium plating efficiency for a bath containing 5 g/l rhodium. Plating efficiency drops rapidly at high sulfuric acid levels and increasing current densities. This is not unexpected since there is an abundance of hydrogen ion to be reduced at the cathode when the acid level is high, and the higher current densities lead to increased hydrogen overvoltages favoring hydrogen reduction.

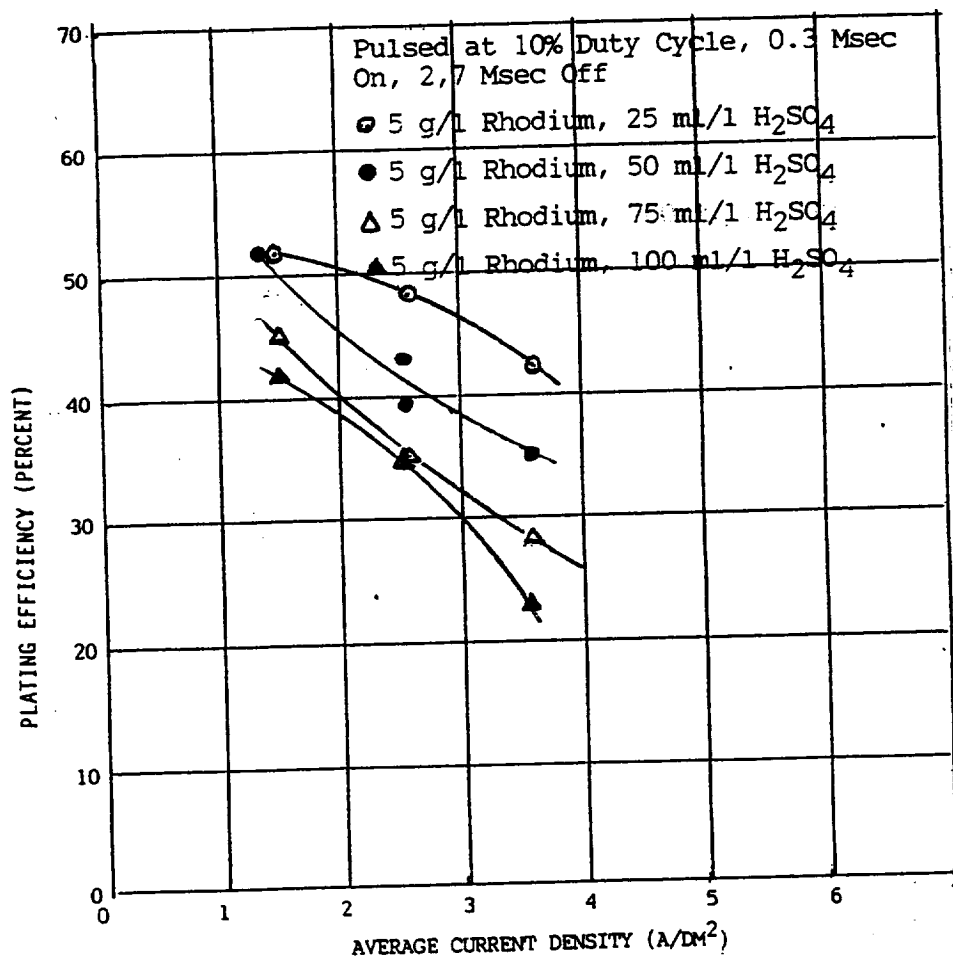


Figure 18. The Effect of Increased Sulfuric Acid Concentration on the Plating Efficiencies in Acid Rhodium Sulfate Baths Containing 5 g/l Rhodium and Pulsed at 10 Percent Duty Cycle.

#### Rhodium Thickness Studies

Rhodium is notoriously difficult to deposit in coherent layers of thicknesses greater than about 25  $\mu\text{m}$ . This, along with the high cost of the metal salts, does not favor the use of this platinum group metal for engineering structures. However, rhodium is good as a screening layer for oxidation protection - it being second to platinum with respect to recession rate in oxygen at elevated

### TABLE XI - RHODIUM THICKNESS STUDY RESULTS

ACID RHODIUM SULFATE BATH PLATING THICKNESS STUDIES													
SPECIMEN NUMBER	DIRECTION	TIME	FORWARD PULSE ON/OFF	REVERSE PULSE ON/OFF	PEAK FWD (msec)	PEAK REV (msec)	CUR. DENS. (Amp/Dm <sup>2</sup> )	REVERSE CUR. DENS. (Amp/Dm <sup>2</sup> )	PLATING TIME (Hours)	AVERAGE CUR. DENS. (Amp/Dm <sup>2</sup> )	DUTY CYCLE (%)	ACUM. DEPOSIT THICKNESS (in)	DEPOSIT APPEARANCE
Bath Concentration Aim: 10 g/L Rhodium and 50 mL/L Sulfuric Acid. Wetting Agent Added (Specimen Nos. 2-9).													
4	FWD. ONLY	DC ONLY	NONE	NONE	3.353	0.000	1.50	3.353	100	0.00236	slightly rough.		
6	FWD. ONLY	0.22/0.44	NONE	NONE	7.890	0.000	1.55	2.630	33	0.00096	Cracks edges & cent.		
7	FWD. ONLY	10.0/20.0	NONE	NONE	4.931	0.000	3.55	1.644	33	0.00161	Microcracks top 80%		
8	FWD. ONLY	3.0/9.0	NONE	NONE	5.918	0.000	2.00	1.479	25	0.00088	Microcracks bot. edge		
1	FWD. ONLY	0.3/0.9	NONE	NONE	8.383	0.000	2.87	2.096	25	0.00124	Microcracking.		
2	FWD. ONLY	0.3/0.9	NONE	NONE	8.383	0.000	2.45	2.096	25	0.00102	Severe microcracks.		
3	FWD. ONLY	0.3/0.9	NONE	NONE	8.383	0.000	2.03	2.096	25	0.00089	fine microcracks.		
9	FWD. ONLY	0.3/2.7	NONE	NONE	26.136	0.000	2.00	2.614	10	0.00157	pebbled; no cracks.		
5	15.0/3.0	0.9/2.7	0.9/2.7	0.9/2.7	14.301	14.301	1.72	3.575	25/25	0.00138	Cracking near edges.		
Bath Concentration Aim: 5 g/L Rhodium and 25 mL/L Sulfuric Acid. More wetting agent added.													
10	FWD. ONLY	0.3/2.7	NONE	NONE	36.492	0.000	2.00	3.649	10	0.00149	Some pits; no cracks		
Bath Concentration Aim: 5 g/L Rhodium and 50 mL/L Sulfuric Acid. Plated 4 Short Runs and 1 Long Run.													
11	FWD. ONLY	0.3/2.7	NONE	NONE	57.204	0.000	2.00	5.720	10	0.00164	Rough; cracked edges		
Bath Concentration Aim: 5 g/L Rhodium and 75 mL/L Sulfuric Acid. Plated in 2 Runs.													
12 Run A	FWD. ONLY	0.3/2.7	NONE	NONE	36.492	0.000	2.00	3.649	10	0.00083	Micropits; no cracks		
Run B	FWD. ONLY	0.3/2.7	NONE	NONE	14.794	0.000	4.00	1.479	10	0.00183	Micropits; no cracks		
Bath Concentration Aim: 5 g/L Rhodium and 100 mL/L Sulfuric Acid.													
13	FWD. ONLY	0.3/2.7	NONE	NONE	54.245	0.000	1.00	5.425	10	0.00054	Micropitted & rough.		
14	FWD. ONLY	0.3/2.7	NONE	NONE	26.136	0.000	4.00	2.614	10	0.00154	Microbumps; no cracks		

temperatures. The objective of the rhodium thickness studies was the development of means to produce deposits of 50  $\mu\text{m}$  (0.002 in) thickness without microcracks extending to the substrate. Table XI summarizes plating data, thickness determinations, and deposit appearance for each specimen produced. Figure 19 illustrates the series of samples in this study after rhodium deposition.

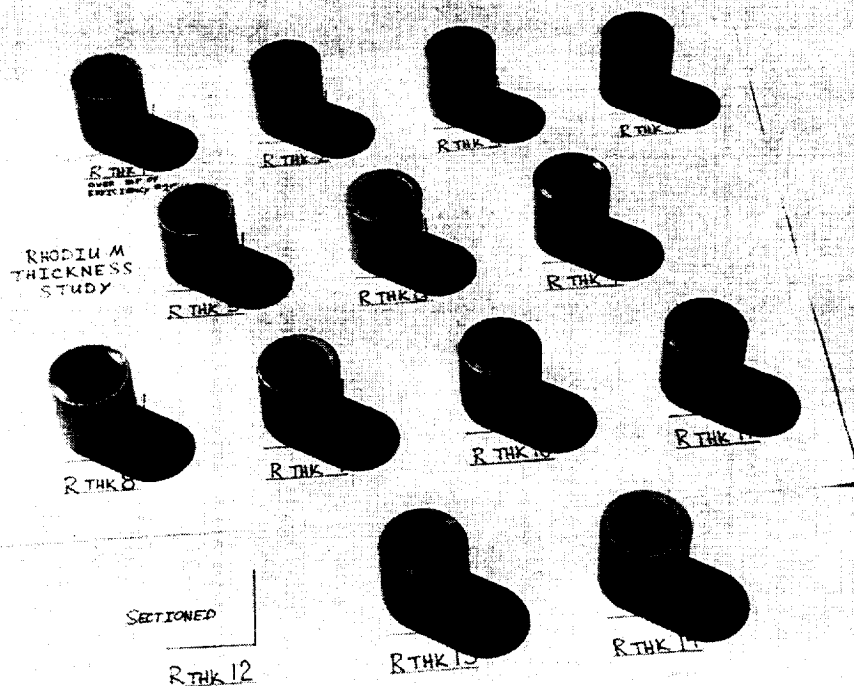


Figure 19. Overview of Rhodium Thickness Study Specimens.

Evaluation of microcracking was made under magnification of about 10X, since such surface defects were visible at this power. The samples deposited from electrolyte containing 10 g/l rhodium and normal sulfuric acid (50 ml/l) showed various degrees of microcracking - most due to high edge current densities. Use of dc plating without pulse appeared to yield rough, crack-free rhodium deposits. Deposits from baths with 5 g/l rhodium were found to be crack-free (using pulsed current) only when the acid content was 75 ml/l or higher.

Specimen No. 12 was sectioned, Figure 20, and found to contain a fairly smooth, coherent layer of rhodium with no visible microcracks. The rhodium appears thicker than the 1.83 mils calculated from weight measurements because the view is near a cylinder edge where buildup is greatest. Underlying coatings to protect the substrate from corrosive attack by the acid rhodium electrolyte are evident in the figure.





Figure 20. Cross-section of Rhodium Thickness Study Specimen No. 12. Magnification 200X.

## Conclusions and Recommendations

### Platinum Deposition

As was found in Table V, deposition of platinum from the highly acidic Platanex III bath proceeds with low efficiency under all plating conditions. Best efficiencies occurred with conventional dc and no pulsing. The bath is sensitive to platinum concentration - excess platinum leading to dark, spongy deposits. pH must be carefully controlled since pH below 1 results in brittle, cracked deposits, and pH above 2 leads to dark, brownish plating. The low efficiency for platinum plating was not surprising, since the literature confirms low efficiencies for all platinum bath types.

From experiences in these studies, the Platanex III bath can not be employed with any form of periodic current reversal unless a thick preplate, free of porosity, has first been applied. Even the use of conventional dc and conventional forward pulse plating present potential problems with attack on the substrate due to low plating efficiencies whereby porosity exists for considerable time (until about 50  $\mu\text{m}$  of deposit is made). Since the end use of the coating involves very high temperatures, gold can not be used as an intermediate coating. Preplates may also be selected based on how the preplate electrolyte affects the particular substrate being used. Figure 21 illustrates a thin Platanex III deposit (12 $\mu\text{m}$ ) over a gold strike over nickel on copper. The significant interruptions within the coating are likely due to corrosive attack through pores in the thin gold strike.

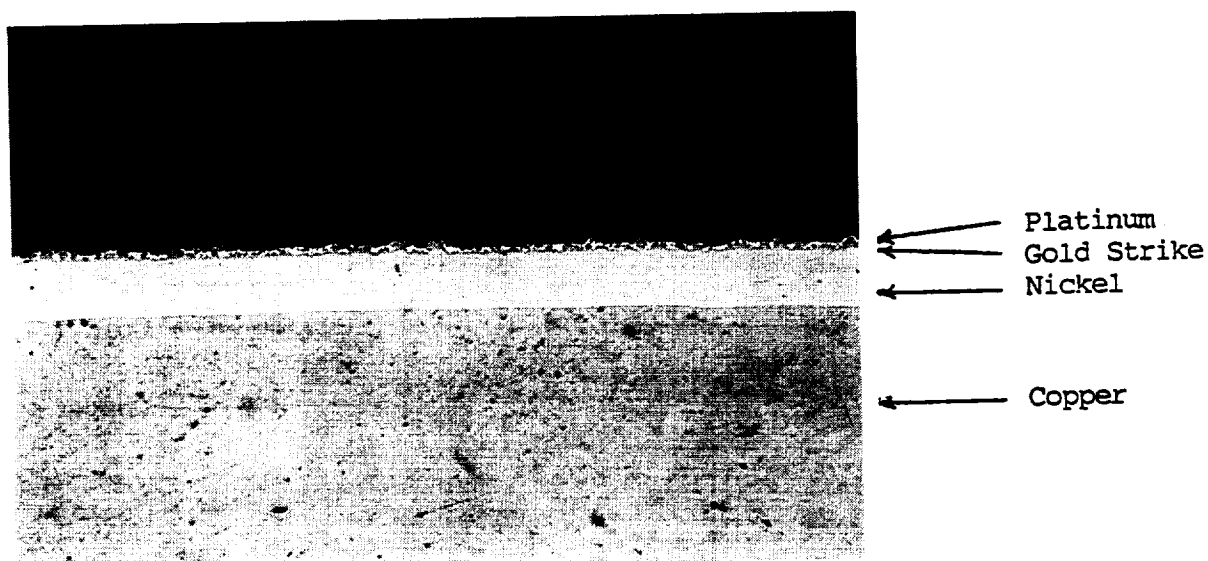


Figure 21. Thin Platinum Over Gold Strike Layer Illustrating Effects of Acidic Attack Through Porous Gold.

Most success with such preplates has been obtained with neutral amino-phosphate complexed platinum chloride type baths and acid rhodium sulfate electrolytes. Use of rhodium sulfate baths may appear to be contradictory because of the high acidity; however, conventional dc plating of rhodium at temporarily high current densities proceeds at such a high plating efficiency that corrosion is minimal, if it occurs at all. During the efficiency study section of this program, the neutral amino-phosphate complexed bath was based on the Technic Platinum AP bath. Later in the program this bath was formulated and operated as follows:

Ammonium Dibasic Phosphate	45 g/l
Sodium Dibasic Phosphate	225 g/l
Dihydrogen Hexachloroplatinate	25 to 50 g/l
Demineralized Water	To 1 liter
Temperature	70 to 80°C
pH	7.2 to 7.8
Current Density, A/dm <sup>2</sup>	1 to 9
Anodes	Platinized Ti
Agitation	Mechanical

In preparing the bath, it is necessary to add the phosphate salts to hot water at less than final volume and bring the solution to about 80°C before adding the platinum salts. The platinum salt is dissolved in demineralized water as a concentrate with the platinum concentration being calculated for later addition purposes. Addition of the platinum concentrate to the hot electrolyte must be made slowly to prevent formation of a green flocculant substance, possibly tetramine tetrachloroplatinate,

which will dissolve with time to form the desired yellow colored electrolyte. pH can be raised with ammonium hydroxide or lowered with phosphoric acid. The bath may appear cloudy upon pH adjustment with ammonium hydroxide, but this does not appear to degrade the deposit quality.

Maintaining the amino-phosphate chloroplatinate bath has reportedly been a major problem which has hindered commercial use of the bath. As platinum is deposited, there is an accumulation of chloride which severely decreases plating efficiency. Operation of the bath with low platinum content (less than 6 g/l platinum) will also yield low efficiency. The platinum concentration can be estimated from the solution color. A new bath with 10 to 16 g/l platinum will be an intense orange-yellow. As platinum is depleted, the color becomes pale yellow followed by crystal clarity as the platinum is further decreased. However, the problem of chloride control is not as simple.

In this investigation a means of resolving the chloride problem was developed. When it is found that platinum replenishment and carbon treatment and filtration do not improve plating efficiency to any degree, the bath can be treated with silver acetate and carbon treated and filtered. The silver acetate precipitates the chlorides as silver chloride. Carbon treatment removes acetates from the silver acetate, and fine filtering removes the silver chloride and carbon. Small amino-phosphate complexed platinum baths can be operated semi-continuously with this treatment for many months.

Since the amino-phosphate and Platanex III baths operate at high temperatures, the problem of fixturing and electrical contacts becomes significant. Many masking materials will not tolerate the bath temperature. There is always a danger of organic contamination from tapes. Teflon fixtures with stainless steel or titanium electrical contacts have proven satisfactory. Platinum has a tendency to creep during plating onto Teflon surfaces and must be removed as an economic measure to prevent wastage of the precious metal.

Continuous deposition of platinum to build a singular layer of 12.5  $\mu\text{m}$  (0.0005 in) is virtually impossible from 1 or 2 liters of electrolyte due to the requirement for periodic carbon treatment, filtration, platinum replenishment, and treatment for chloride removal. Very thick deposits (up to 100  $\mu\text{m}$ , or 0.004 in) were made in seventeen plated layers from an amino-phosphate complexed chloroplatinate bath. The key to this method is the production of high integrity bonds between the platinum layers as will be described later in this report. An illustration of such a sample with platinum plated over a thin rhodium interface on a Mo-47Re substrate will be found in Figure 22. This specimen was plated by Electroformed Nickel, Inc. and oxidation tested at 1260°C for

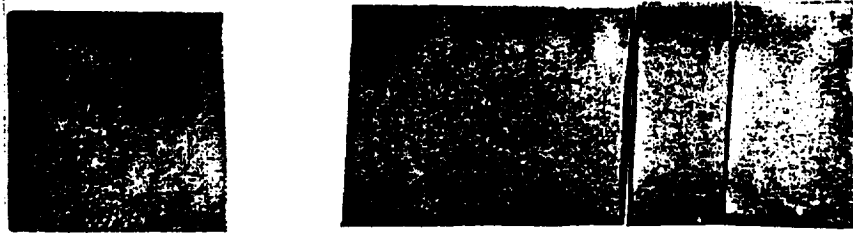


Figure 22. Sectioned Specimen of Mo-47%Re Alloy Plated With 17 Layers of Platinum (100  $\mu$ m) Over Rh Interface and Oxidation Tested at 1260°C for 30 Hours in Air.

30 hours in air by Pratt & Whitney, West Palm Beach, Florida with good performance.

Continued use of the amino-phosphate complexed neutral platinum bath is recommended. However, scaling the bath to a much larger size is advised in order to provide continuous filtering and to accommodate longer plating times without excessive consumption of platinum metal on a grams per liter basis. Pulse plating at duty cycles under sixty percent and pulse plating with periodic current reversal are not recommended for efficiency reasons.

#### Rhodium

Rhodium plating efficiencies are highly dependent on bath composition. High rhodium metal content (10 g/l) and moderate sulfuric acid concentration (< 50 ml/l) favor plating efficiencies of 90% or more. Pulse plating may be used with satisfactory plating efficiency if the pulse duty cycle is 75% or higher. In general, the longer pulse durations (longer "on" times) for a duty cycle resulted in higher efficiencies. Lowering the rhodium metal content or increasing the sulfuric acid concentration lowers plating efficiencies. Use of 50%, or lower, pulse duty cycles results in significant efficiency reduction.

As with the amino-phosphate complexed neutral platinum bath, the metal content of the acid rhodium sulfate bath can be visually assayed by color between formal analyses. A high rhodium metal bath will be dark red-brown in appearance - similar in color to root beer. As rhodium is consumed, the color lightens and the solution becomes more transparent. Sulfuric acid is determined by conductometric titration with 0.1N NaOH on a pH meter. As the

rhodium is depleted from plating, it is replenished by additions from the concentrate. Unfortunately, the concentrate contains sulfuric acid to prevent rhodium precipitation. As new rhodium is added to the bath, the sulfuric acid concentration is increased automatically. Unchecked buildup of acid leads to rapid deterioration of plating efficiency and potential for chemical attack on the substrate. This is particularly true for small baths where more frequent rhodium additions must be made for each ampere-hour of current passed. Sulfuric acid contents as high as 200 ml/l have been observed by personnel performing thick rhodium deposition in later stages of this program.

A means for sulfuric acid control was developed in this program which permits continued use of the electrolyte for several months of plating. As sulfuric acid exceeds 55 ml/l, barium carbonate is added - reacting with the acid to produce barium sulfate and carbonic acid. The barium sulfate is precipitated and filtered out while the carbonic acid decomposes under heat to water and carbon dioxide.

Stress problems were a major cause of coating failures in early attempts to deposit thick rhodium. Coatings as thick as 12.5  $\mu\text{m}$  (0.5 mil) were possible with the Technic Rhodium TP bath which was believed to contain magnesium sulfamate (or sulfate) stress reducing agent. Additions of magnesium sulfamate to 60 g/l were not very effective in preventing cracking of deposits beyond 25  $\mu\text{m}$  (1 mil). Addition of selenic acid to the rhodium electrolyte proved very effective in reducing stress. Analysis of deposits of rhodium from such baths (performed by TRW, Redondo Beach, CA) disclosed that selenium was not codeposited with the rhodium. It was also found that reasonably thick rhodium deposits could be made by layering 12.5  $\mu\text{m}$  deposits in a manner similar to that employed for thick platinum plating. The key to this technique was the ability to produce high integrity rhodium to rhodium bonds as described later in this report.

Since the rhodium bath operates at 45° to 55°C, the problems of masking, electrical contacts, and fixturing are lessened when compared to platinum. However, the bath is highly acidic and any organics extracted from masking tapes are extremely degrading in respect to deposit stress. If tapes are used, it is recommended that polyester be employed. The bath should be frequently carbon treated. Since significant hydrogen is generated when rhodium plating, the use of sodium laurel sulfate as a wetting agent is recommended. This must be replaced each time the bath is carbon treated. Solution agitation is essential in thick rhodium plating to assist in hydrogen removal at the cathode surface.

It is recommended that larger baths be employed for any Phase III work to reduce rate of rhodium depletion based on ampere-hours of plating. Such bath sizes would permit continuous filtration and

acid buildup would be slower on a volumetric basis. Selenic acid should be used for stress relief and the electrolyte should be pumped through a spray(s) for improved agitation and hydrogen removal from the cathode surface. Besides the plating efficiency decrease associated with periodic current reversal, this mode is prone to deposit rhodium on the platinized anodes during reversals - a serious waste of rhodium. PR is also not recommended for platinum plating for the same reasons.

**TASK I - INVESTIGATION OF PULSED CURRENT DEPOSITION  
OF OXIDATION RESISTANT NOBLE METALS  
PART B - RUTHENIUM, IRIDIUM, AND RHENIUM ELECTRODEPOSITS**

**Ruthenium - State of the Art**

According to Raub [14], ruthenium is hard, brittle, and easily oxidizes. These factors limit its use. It was included in this program as a possible metal for alloying with other platinum group metals only because of its low cost. All ruthenium electrolytes are based on solutions of simple ruthenium salts or on ruthenium nitrosyl derivatives. Typical examples are ruthenium sulfamate, ruthenium phosphate, ruthenium sulfate, or ruthenium chloride. They operate in wide ranges of current densities from 1 to 10 A/dm<sup>2</sup> at temperatures of 50° to 90°C and current efficiencies of 50 to 90%. Table XII provides compositions and operating conditions for two plating solutions. The deposits are hard and highly stressed, making it difficult to obtain crack-free layers at greater thicknesses.

Reid and Blake [21] studied wide varieties of ruthenium plating solutions and concluded that the nitrosyl sulfamate bath offered the most useful solution, furnishing smooth, bright deposits to 10.5 μm (0.0002 in) thickness over a wide range of operating conditions. They reported cathode efficiency as low (10 to 20%) and stresses in the range of 40 to 60 ksi tensile. Cracks were usually present in thicknesses greater than 2.5 μm (0.0001 in). They also noted that the best deposits could be obtained from a molten salt bath composed of an eutectic mixture of sodium and potassium salts; thicknesses to 38 μm (1.5 mils) were mentioned.

**Ruthenium Plating Efficiency Studies**

A Sel-Rex Ruthenex SP bath was used in this work. The solution was prepared from Ruthenex SP Make-up Concentrate containing 16 g/l of ruthenium as a sulfamate. Diluting 250 ml of the starting concentrate with 750 ml of deionized water provided the one liter bath. The facility was the same as previously used for rhodium and platinum studies. The recommended operating range for this bath and range of chemical composition is:

**TABLE XII - RUTHENIUM PLATING SOLUTIONS**

Constituent or condition	Amount or value
<b>General-purpose solution</b>	
Ruthenium (as sulfamate or nitrosyl sulfamate), g/L (oz/gal)	5.3 (0.7)
Sulfamic acid, g/L (oz/gal)	8 (1.1)
Anodes	Platinum
Temperature, °C (°F)	
Sulfamate solution	27-60 (80-140)
Nitrosyl sulfamate solution	21-88 (70-190)
Current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	1-3 (10-30)
Current efficiency, %	20
Time to plate thickness of 0.003 mm (0.0001 in.)	30-40 min at 2 A/dm <sup>2</sup> (20 A/ft <sup>2</sup> )
<b>Flash-plating solution for decorative deposits</b>	
Ruthenium (as nitroso salt), g/L (oz/gal)	2.0 (0.3)
Sulfuric acid, g/L (oz/gal)	20 (2.7)
Current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	2-3 (20-30)
Temperature, °C (°F)	50-80 (120-180)

Note: Both solutions require a flash-plated undercoat of gold or palladium.

Ruthenium	Nominal	Range
Temperature	5 g/l	4 to 6 g/l
pH	70°C	60 - 80°C
Agitation	1.8	1.5 - 2.0
Anode to Cathode Ratio	Light solution movement.	
Cathode Current Density	4 to 1 or higher	
Anodes	1.075 A/dm <sup>2</sup> (10 ASF)	
	Platinized titanium	

Specimens were short lengths of thick wall OFHC tube plated with nickel and struck with gold for corrosion protection. Fixturing and electrical contacts were similar to those used in platinum studies previously described. To lessen sample preparation and fixturing time, most of the test cylinders were plated in several consecutive runs, each with a variation of current density or pulse duty cycle. Weighings and surface inspection results were recorded for each run. Table XIII summarizes plating parameters, weight change data, calculated plating efficiencies, and surface appearance of the sample after each plating run. Figure 23 shows the ruthenium plated cylinders used in the efficiency and thickness studies. Specimen No. 48 in this illustration was sectioned for coating evaluation. This sample was used in both the plating efficiency studies and the thickness study.

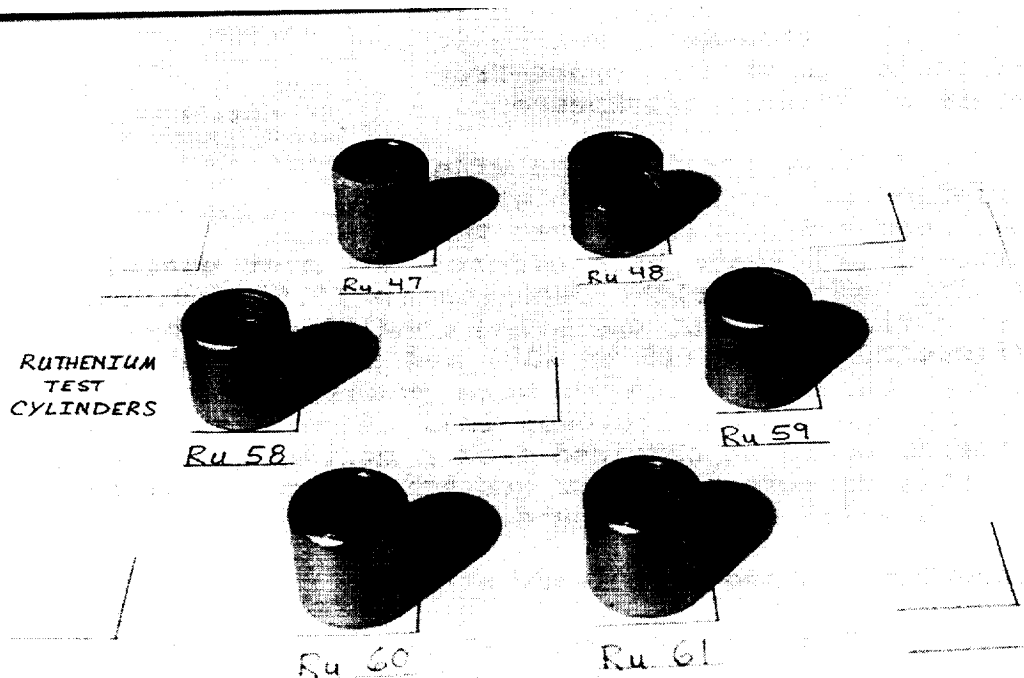


Figure 23. Appearance of Test Cylinders After Ruthenium Plating for Efficiency and Thickness Studies





Figure 24 is a graphical presentation of ruthenium plating efficiencies for a pulsed current duty cycle of 10 percent at various current densities. Lengthening the pulse "on" time from 0.1 to 0.2 milliseconds appears to slightly improve plating efficiency. Figure 25 shows that plating efficiencies are slightly improved by increasing the pulsed current duty cycle from 10 percent to 20 percent.

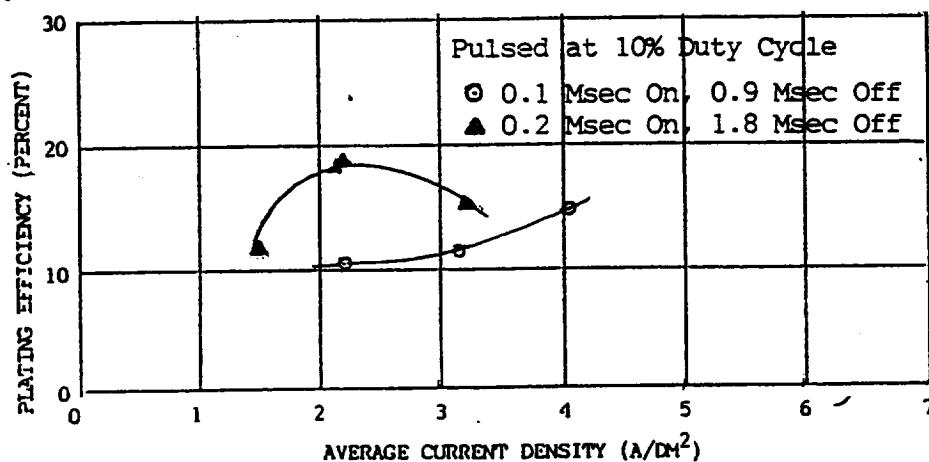


Figure 24. Ruthenex SP Bath Plating Efficiencies Using Pulsed Current With a 10 Percent Duty Cycle.

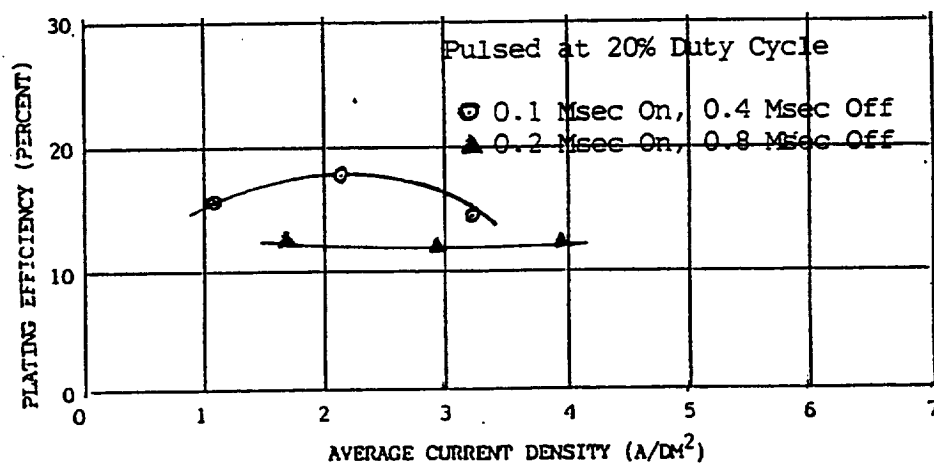


Figure 25. Ruthenex SP Bath Plating Efficiencies Using Pulsed Current With a 20 Percent Duty Cycle.

These figures show ruthenium plating efficiencies to be consistently within the range of 10 to 20 percent using pulsed plating duty cycles of 20 percent or less. Since the literature reports similar performance for conventional dc plating of ruthenium, it is concluded that further exploration of pulse plating effects on plating efficiency would yield little, if any, useful data. On this basis, it was determined that studies of pulsed current duty cycles in the range of 60 to 80 percent would not be pursued.

TABLE XIV - RUTHENIUM PLATING THICKNESS STUDIES

SPECIMEN NUMBER AND RUN NUMBER	SEL-REX RUTHENEX SP RUTHENIUM PLATING THICKNESS STUDIES				RUTHENIUM PLATING THICKNESS STUDIES				RUTHENIUM PLATING THICKNESS STUDIES			
	FORWARD PULSE ON/OFF (Milli. sec)	PEAK FORWARD CUR. DENS. (Amp/Dm)	CALCULATED AVERAGE CUR. DENS. (Amp/Dm)	PLATING TIME (Hours)	ACCUM. DEPOSIT WEIGHT (grams)	DUTY CYCLE (%)	DEPOSIT THICKNESS (in)	DESCRIPTION OF SURFACE AND COMMENTS	ACCUM. DEPOSIT THICKNESS (in)	DESCRIPTION OF SURFACE AND COMMENTS	ACCUM. DEPOSIT THICKNESS (in)	DESCRIPTION OF SURFACE AND COMMENTS
48-1	0.1/0.4	10.849	2.170	0.50	0.0487	20.0	0.0007	Matte gray.	0.0007	Matte gray.	0.0007	Matte gray.
48-2	0.1/0.4	16.274	3.255	0.50	0.1072	20.0	0.0016	Semi-bright gray.	0.0016	Semi-bright gray.	0.0016	Semi-bright gray.
48-3	0.1/0.8	43.396	2.284	0.50	0.1262	11.1	0.0019	Microroughness.	0.0019	Microroughness.	0.0019	Microroughness.
48-4	1.0/10.0	11.835	1.076	0.50	0.1462	9.1	0.0022	Microroughness.	0.0022	Microroughness.	0.0022	Microroughness.
48-5	0.2/1.8	21.698	2.170	0.50	0.1952	10.0	0.0030	Bright and smooth.	0.0030	Bright and smooth.	0.0030	Bright and smooth.
48-6	0.2/1.8	10.849	1.085	2.00	0.3038	10.0	0.0046	Bright; some microroughness.	0.0046	Bright; some microroughness.	0.0046	Bright; some microroughness.
48-7	0.2/1.8	10.849	1.085	1.00	0.4595	10.0	0.0070	Pits starting; incr. roughness.	0.0070	Pits starting; incr. roughness.	0.0070	Pits starting; incr. roughness.
48-8	0.2/1.8	10.849	1.085	2.50	0.7329	10.0	0.0112	Small microcracks starting.	0.0112	Small microcracks starting.	0.0112	Small microcracks starting.
51	0.1/0.4	5.425	1.085	2.72	0.1194	20.0	0.0010	Small scattered cracks noted.	0.0010	Small scattered cracks noted.	0.0010	Small scattered cracks noted.

Ruthenium plating thickness studies were limited to two specimens as shown in Table XIV because of microcracking which was not unexpected. A metallographic examination of Specimen No. 48, which contained eight layers of ruthenium, was made. Figure 26 shows the great extent of cracking in this coating. Deposits of this thickness with such defects would be of little use in elevated temperature oxidation protection.

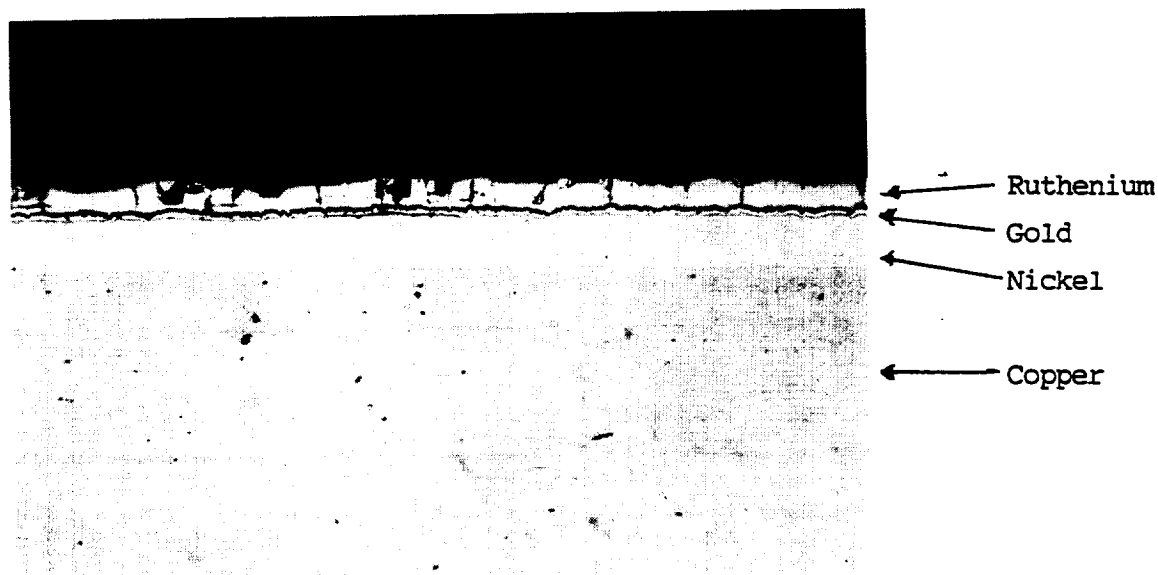


Figure 26. Cross-section of Ruthenium Thickness Specimen No. 48. Magnification 200X.

#### Iridium - State of the Art

Lowenheim [9] cited the status of iridium plating (as of 1978) as having little, if any, commercial practice. He noted that sound deposits were only obtained from molten salt baths - aqueous bath deposits being cracked when over  $1\text{ }\mu\text{m}$  and bath efficiencies being very low. Raub [14] states that essentially no electrolytes are available that can deposit iridium from aqueous solutions at reasonable thicknesses and with satisfactory properties. Known aqueous electrolytes are mostly based on chloro-iridic acid. The bath is highly acidic and operates at  $80^{\circ}\text{C}$  with a current density of  $0.15\text{ A/dm}^2$  (1.4 ASF). As thickness exceeds  $1\text{ }\mu\text{m}$ , the layers become cracked. Current efficiency is reported to be about 50%, and the low current density plating rate approaches  $1\text{ }\mu\text{m/h}$ .

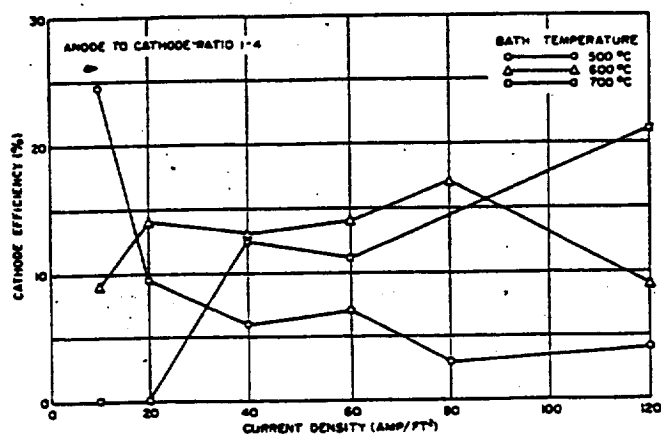
Raub describes successful iridium deposition from fused salts. The solution was prepared by passing alternating current between two electrodes of iridium suspended in the melt. The melt was a eutectic mixture of potassium and sodium cyanides with a melting point between  $500$  and  $564^{\circ}\text{C}$  ( $930$  and  $1050^{\circ}\text{F}$ ). He points out that these baths have not proven usable in commercial practice.

Conn [22] claimed development of an aqueous iridium plating bath with efficiencies and deposit thicknesses sufficiently high as to be suitable for commercial use. The bath was composed of iridium (III) chloride tetrahydrate and sulfamic acid. A current density of  $0.1 \text{ A/dm}^2$  was used. Auxiliary iridium electrodes were used to supply iridium to the electrolyte by passing alternating current through them at a current density of 20 to  $400 \text{ A/dm}^2$ . Direct current for plating was from a second power supply. A maximum thickness of  $25 \text{ }\mu\text{m}$  (1 mil) was claimed, but the thicker deposits were highly stressed and cracked. No successful duplication of this work by other investigators has been reported.

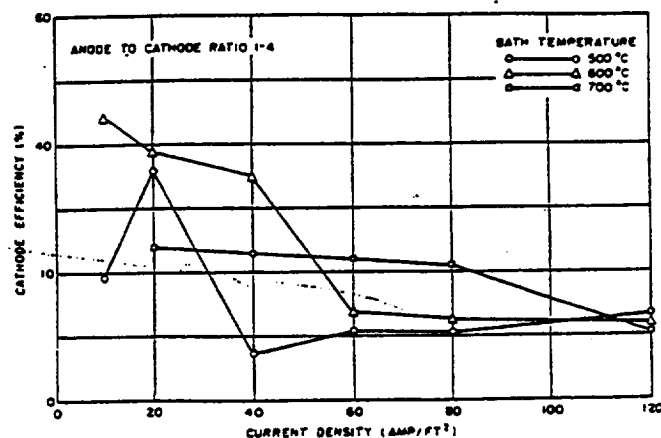
Tyrrell [23] described a multitude of iridium electrolytes examined by INCO, London, UK. Included in this study was a promising electrolyte prepared by dissolving hydrated iridium dioxide in boiling hydrobromic acid. He claimed that the bath was stable, and the deposits obtained were bright and adherent. They were reportedly somewhat porous and subject to cracking at thicknesses greater than  $1 \text{ }\mu\text{m}$ . Thicknesses could be obtained up to  $10 \text{ }\mu\text{m}$  on a variety of base metals. At preferred operating conditions of 5 g/l iridium,  $75^\circ\text{C}$ , and  $0.15 \text{ A/dm}^2$ , a current efficiency of 65% was possible on most substrates.

McNamara [24] claimed deposition of iridium from an aqueous bath containing chloriridic acid,  $\text{H IrCl}_6$ . The acid ionizes with the formation of a complex  $\text{IrCl}_6^{3-}$  anion.<sup>6</sup> The best plating conditions favored a metal concentration of 10 g/l, with the bath operated at  $60^\circ\text{C}$  and a current density of  $6.6 \text{ A/dm}^2$  for a cathode efficiency of 6 percent. Dropping the current density to  $2.2 \text{ A/dm}^2$  led to a 14 percent cathode efficiency. The solution pH was 2.

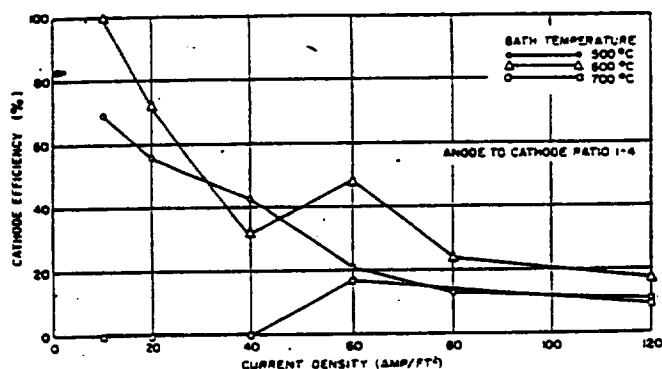
Withers and Ritt [25] obtained good electrodeposits of iridium using 800 to 1000 mg of iridium in 200 g of a fused salt (5.33 to  $6.66 \text{ g/l}$ ) consisting of 70 parts by weight of sodium cyanide and 30 parts by weight of potassium cyanide at  $600^\circ\text{C}$ . Best deposits were obtained at  $1.07$  to  $2.15 \text{ A/dm}^2$  (10 to 20 ASF). Argon gas was supplied over the melt surface to minimize oxidation of salts and electrodes. Experiments were conducted with melt temperatures of  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ , and  $700^\circ\text{C}$ . To charge the electrolyte with an iridium complex, two iridium electrodes were placed in the melt and electrolyzed with 60 cycle alternating current at  $1.07 \text{ A/dm}^2$  (10 ASF). Weighing the iridium electrodes before and after electrolyzing enabled calculation of the amount of iridium added to the bath. Higher than expected anode efficiencies in the ac electrolysis led to speculation that iridium may have dissolved in lower valence states, as well as the desired trivalent form. A most useful result of their work was the published effect of current density and melt temperatures on cathode current efficiencies, Figure 27. They noted that the melt had a tendency to creep at temperatures above  $600^\circ\text{C}$  and made deposition work more difficult.



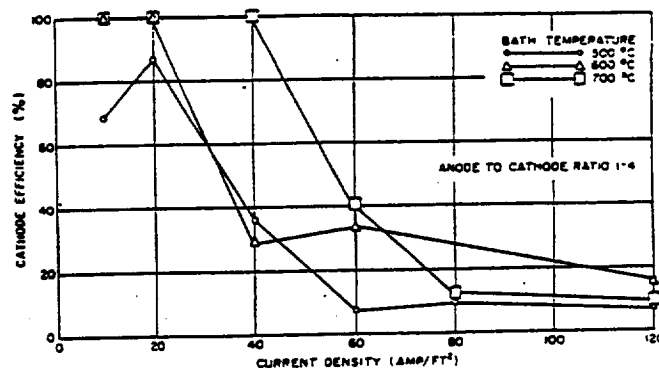
a. Iridium Concentration  
0.33 to 0.66 g/l.



b. Iridium Concentration  
1.00 to 1.33 g/l.



c. Iridium Concentration  
2.00 to 3.33 g/l.



d. Iridium Concentration  
5.33 to 6.66 g/l.

Figure 27. Effect of Current Density and Temperature on Cathode Efficiency of Iridium Plating from Withers and Ritt [25].

Macklin and LaMar [26] investigated deposition of iridium from a fused cyanide bath similar to that used by Withers and Ritt. The bath was operated at 600°C, an iridium concentration of 12 g/l, a current density of 1.6 to 2.7 A/dm<sup>2</sup> (15 to 25 ASF), and periodic current reversal was employed. They encountered dendritic "tree-like" grains in trying to make thick deposits (over 72  $\mu$ m, or 6 mils). They concluded that it was necessary to deposit a thin coating of 25 to 75  $\mu$ m (1 to 3 mils) initially and heat treat the specimen in hydrogen at 1200°C. This coating was sanded smooth and air blasted to remove particles. An anneal at 1200°C was then made and the next deposition made from the fused salt bath. They also considered that multiple coatings of iridium with intermediate sanding would provide better thickness distribution.

### Iridium Plating Studies - Aqueous Baths

Substrate specimens were copper plated with nickel and overplated with gold as in prior plating efficiency studies. Three plating baths, each one liter in volume, were prepared as follows:

	Ir	IrCl <sub>3</sub>	Sulfamic Acid
Bath No. 1	5 g/l	9.7 g/l	25 g/l
Bath No. 2	5 g/l	9.7 g/l	50 g/l
Bath No. 3	10 g/l	19.4 g/l	50 g/l

Auxiliary anodes of small surface area were used with high alternating current densities (in accordance with Conn's recommendations) in an effort to build up the preferred iridium complexes in the baths. Sixteen plating test runs were made as described in Table XV. None of the samples exhibited cohesive iridium, although a metallic appearing film was noted on some specimens which could be easily wiped away. Use of aqueous iridium chloride baths was abandoned in favor of fused salt baths. Figure 28 illustrates an aqueous iridium plating bath.

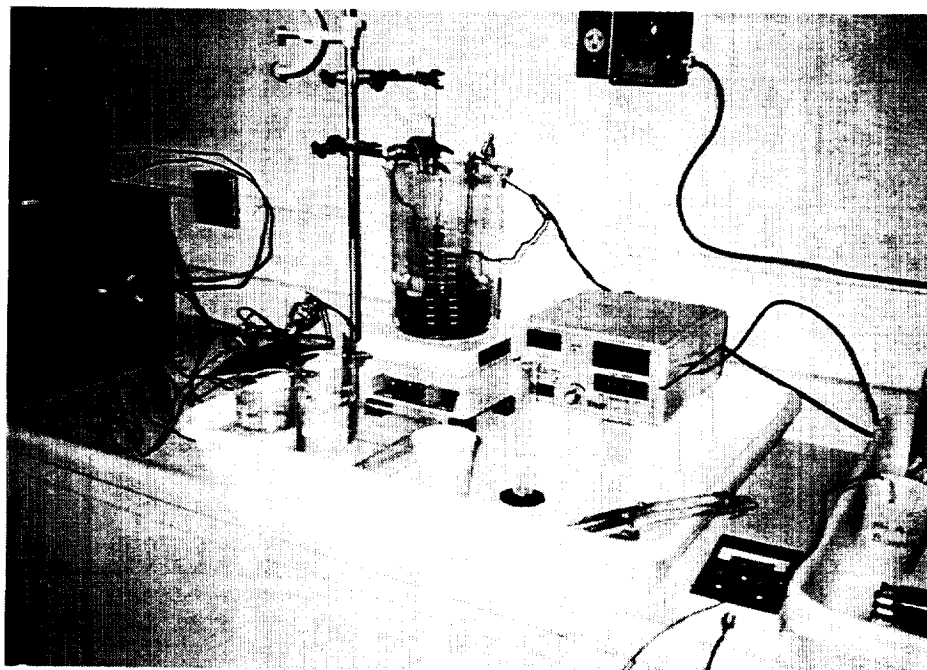


Figure 28. Aqueous Iridium Plating Bath With Pulse Plating Power Supply and Hot Plate-Stirrer.

### Iridium Plating Studies - Fused Salt Bath Facilities

Deposition of metals from fused salt baths is unconventional in that special containment equipment and heating capabilities are required that are totally unlike facilities used for aqueous deposition. A fused salt facility must be designed and installed from commercially available components. Support equipment must

TABLE XV - PLATING TRIAL RESULTS FROM AQUEOUS IRIIDIUM BATHS

SULFAMATE COMPLEXED IRIIDIUM CHLORIDE PLATING EFFICIENCY STUDIES												
SPECIMEN NUMBER	DIRECTION TIME	FORWARD PULSE		REVERSE PULSE		PEAK		PLATING TIME (Minutes)	CALCULATED AVERAGE CUR. DENS. (Amp/Dm)	BATH TEMP. ( C )	ACCUM. DEPOSIT THICKNESS (In)	DEPOSIT APPEARANCE
		ON/OFF (MilliSec)	ON/OFF (MilliSec)	ON/OFF (MilliSec)	ON/OFF (MilliSec)	FWD CUR. DENS. (Amp/Dm)	REVERSE CUR. DENS. (Amp/Dm)					
Bath No. 1: 5 g/L Iridium, 25 g/L sulfamic Acid.												
Ir 01	FWD. ONLY	0.1/0.9	NONE			4.931	0.000	20.00	0.493	55-56 C	0.0000	No Ir deposited.
Ir 02	FWD. ONLY	2.5/3.0	NONE			2.170	0.000	20.00	1.184	60-61 C	0.0000	No Ir deposited.
Ir 03	8.0/10.0	3.0/1.0	1.0/9.0			0.657	4.930	20.00	0.493	61-62 C	0.0000	No Ir deposited.
Bath Temperature Increased to About 70 C.												
Ir 04	FWD. ONLY	DC ONLY	FWD. ONLY			0.020	0.000	30.00	0.020	67-69 C	0.0000	No Ir deposited.
Ir 05	2.0/1.0	DC ONLY	DC ONLY			0.740	0.493	20.00	0.493	68-69 C	0.0000	No Ir deposited.
Bath Temperature Increased to About 90 C.												
Ir 06	FWD. ONLY	3.0/3.0	FWD. ONLY			0.986	0.000	20.00	0.493	88-90 C	0.0000	No Ir deposited.
Bath Temperature Decreased to About 80 C, Sulfamic Acid Increased to 50 g/L.												
Ir 07	FWD. ONLY	1.0/6.0	FWD. ONLY			3.452	0.000	20.00	0.493	82 C	0.0000	No Ir deposited.
Bath Temperature Changed to About 85 C, Iridium Increased to 10 g/L.												
Ir 08	FWD. ONLY	1.0/3.0	FWD. ONLY			1.973	0.000	60.00	0.493	85-87 C	0.0000	No Ir deposited.
Bath Temperature Changed to About 75 C.												
Ir 09	FWD. ONLY	8.3/8.3	FWD. ONLY			0.986	0.000	60.00	0.493	75-78 C	0.0000	No Ir deposited.
Ir 10	FWD. ONLY	8.3/8.3	FWD. ONLY			1.282	0.000	60.00	0.641	73 C	0.0000	purple film formed.
Ir 11	FWD. ONLY	8.3/20.3	FWD. ONLY			1.282	0.000	60.00	0.372	72-75 C	0.0000	Metallic film under purple film;rubs off
Ir 12	FWD. ONLY	8.3/20.3	FWD. ONLY			2.466	0.000	30.00	0.716	81-85 C	0.0000	Like Ir 11.
Ir 13	FWD. ONLY	0.1/0.4	FWD. ONLY			3.452	0.000	30.00	0.690	78 C	0.0000	Like Ir 11.
Ir 14	FWD. ONLY	1.1/3.3	FWD. ONLY			2.959	0.000	30.00	0.740	78-79 C	0.0000	No Ir visible.
Ir 15	FWD. ONLY	20.0/33.0	FWD. ONLY			1.923	0.000	30.00	0.726	78 C	0.0000	Like Ir 11
Ir 16	FWD. ONLY	75.0/7.5	FWD. ONLY			3.156	0.000	30.00	2.869	78 C	0.0000	Like Ir 11.



be improvised based on requirements for protection of personnel, the furnace, and the crucible containing the melt. Flow of a gas such as argon over the fused salt is essential for protection of equipment from oxidation and slag formation in the melt. Figure 29 shows the fused salt facilities.



Figure 29. View of the Two Fused Salt Electroplating Facilities.

Both fused salt baths are on carts to permit relocation in event of a crucible leak. Each unit contains a vertical well furnace, a controller for precise temperature control, a dc or pulse power supply, temperature monitoring thermocouples, and an argon supply system. The furnaces were supplied by The Mellen Company of New Hampshire. During the program, four furnaces were used:

1. 5" diameter x 12" high heating zone (2 each).
2. 6" diameter x 12" high heating zone (1 each).
3. 7" diameter x 6" high heating zone (1 each).

The furnaces were operated with 240 volt input for heating and had a maximum temperature rating of 1200°C. Since a high attention level must be devoted to the furnace operation, no more than two furnaces were operated at any time. This resulted in a need for only two furnace controllers. One unit was a Eurotherm Model 94 furnace controller equipped with a Eurotherm Model 92 alarm controller. The other unit was a Honeywell UDC furnace controller equipped with a Eurotherm Model 92 alarm controller. Both of

the furnace controllers were capable of ramping up rates of 60°C per hour; however, only the Honeywell unit was capable of ramping down at similar rates. Slow ramp rates were used to avoid cracking of crucibles from thermal shock. The crucible manufacturer's maximum recommended heating rate for high alumina hardware was 150°C per hour. A ramping rate of 60°C was used in this work.

For power supplies, two Kraft Dynatronics Model DPR 20-30-100 and one Model DP 10-1-3 were used. The DPR 20-30-100 rectifier has conventional dc, pulsed dc, periodic reverse, and pulsed periodic reverse capability with maximum outputs of 20 volts, 30 amperes (average current), and 100 amperes (peak current). The DP 10-1-3 has conventional dc and forward pulsed current capability only with maximum outputs of 10 volts, one ampere (average), and 3 amperes (peak). The DPR 20-30-100 is shown in Figure 30.

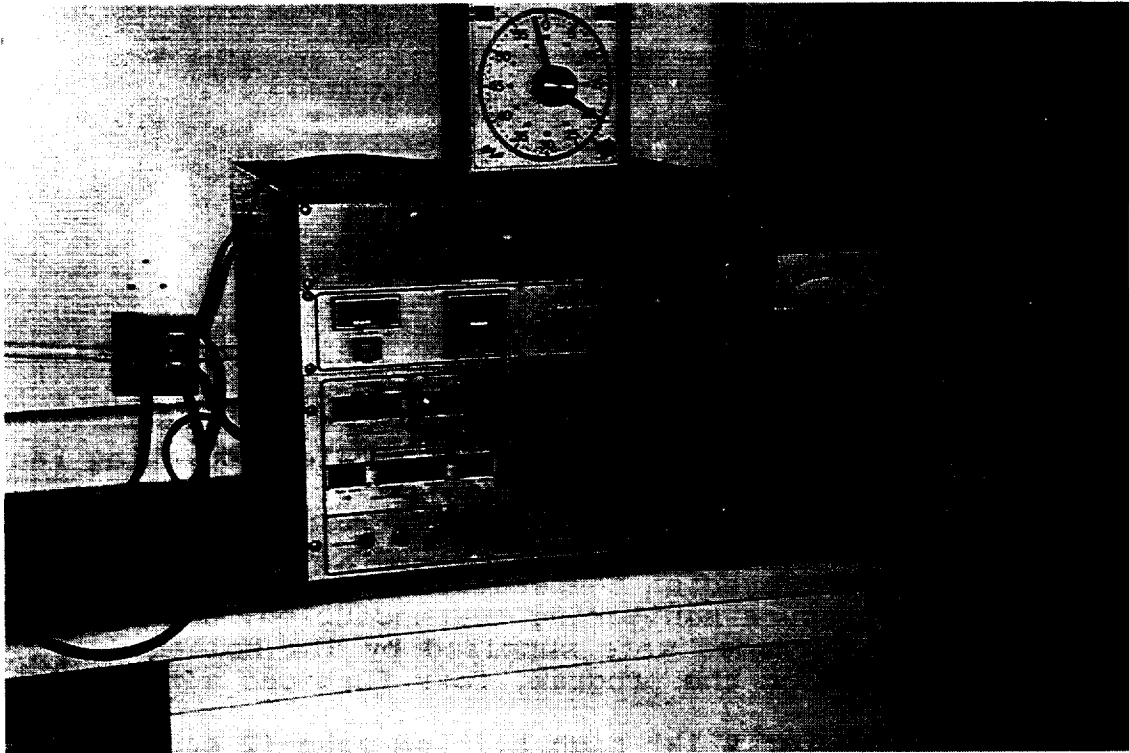


Figure 30. Model DPR 20-30-100 Pulsed PR Power Supply.

Crucible selection was of primary importance in the program. The importance of withstanding thermal shock was very important since the fused salt was to be a mixture of alkali metal cyanides at temperatures to 650°C. Although secondary to safety, the cost of crucibles was considered; they are very expensive and often have long lead times in procurement. Several commercially available high alumina or mullite crucibles were evaluated and the following comments pertain to performance and how each crucible was used in the program:

1. Coors Ceramicon Designs supplied Model AD-998 high alumina ceramic crucibles in 750, 1000, 1500, and 2400 ml capacities. These were used for primary melt containment. About one dozen were lost due to cracking while heated. It was believed that the near flat bottomed shape of this type of crucible resulted in a high stress concentration which was too susceptible to thermal shock. Use of this design was discontinued in the program.
2. Vesuvius McDanel supplied high form, alumina crucibles in 1000 and 2000 ml capacities. These crucibles are designed with a large bottom radius which makes the bottom actually spherical. They have demonstrated a greater immunity to cracking than the more flat bottomed varieties.
3. B&B Refractories furnished mullite tapered crucibles in 1000 and 2000 ml capacities. These crucibles were unsuitable for primary containment vessels, but they were used as fixturing materials because of their heat resistant, electrical insulating, and absorbent properties. Sections were cut with carbide blades for use as spacers, seals, insulators, and spill containment cups.
4. In-house electroformed nickel and nickel-manganese alloy crucibles were made for use as back up primary melt containment vessels. They served to prevent leaking cyanide from destroying the furnace in event of a cracked ceramic crucible.

#### **Iridium Plating Studies - Experiences and Observations**

All of the molten cyanide plating baths used in this program were composed of 70 weight percent sodium cyanide and 30 weight percent potassium cyanide. The density of this mixture is approximately 1.5 g/ml. A molten kilogram of this eutectic mixture has a volume of about 667 ml. This cyanide mixture melted at about 485°C. However, it was found that the melt operated best at 610° to 650°C for lower viscosity. At temperatures above 640°, this melt mixture became very mobile - creeping up crucible walls and migrating onto the furnace walls. This is similar to the experiences of Macklin and LaMar [26].

Furnace temperature setpoints were much higher than the desired melt temperatures because of thermal losses due to conduction and radiation in the furnace and the flowing argon blanket. Furnace temperature setpoints also varied with different crucible combinations and melt volumes. This temperature was generally 120 Centigrade degrees higher than the desired melt temperature. It was found desirable to keep each melt at its full operating temperature until all work with that melt was completed. It was also found that molten cyanide solidified on room temperature parts

immersed in the bath. This blocked crucial initial deposition. To avoid this problem, parts were pre-heated in a second furnace, either in a crucible filled with molten cyanide, or in a heated crucible under argon. Actual fused salt temperatures were measured with a 12 inch long Inconel thermocouple probe.

For iridium, or any other fused salt plating bath, there is a unique concentration of dissolved metal (ion complexes) which produce the best plating efficiency. Maintaining this correct concentration was found to be critical to successful deposition. The concentration of iridium in the melt was observed to increase continuously during plating operations. This was believed due to the fact that (1) plating was far less than 100 percent efficient as noted by Withers and Ritt for iridium concentrations under 3.5 g/l and melt temperatures around 600°C, Figure 27; (2) chemical attack on the anodes at this high temperature; and (3) extremely high anodic current densities. Withers and Ritt employed anode to cathode area ratios of 1:4. In studies in this program, it was necessary to use even more unfavorable ratios because of the configurations of the end use parts to be plated and the high costs and lead times for iridium anode stock.

Tracking the metal concentration in a melt involved making daily measurements of anode weight losses and cathode weight gains. To adjust iridium concentrations downwards, a calculated weight of high concentration salts was ladled out and replaced with fresh mixed cyanide salts. Two methods of adding iridium to the bath were used: (1) passing 60 cycle alternating current between two iridium anodes, and (2) passing direct current between two iridium anodes. The former method dissolved iridium into the melt at a faster rate.

Anodes were removed after each plating run to prevent chemical attack when not in use. Where possible, anodes were suspended in the melt using wire of the same material as the anode. Since the wires were thin, they were kept out of the melt itself to prevent breakage and loss of the anode into the melt. As an additional precaution, several strands of wire were used. In an effort to decrease the rate of iridium anode consumption leading to iridium buildup in the melt, use of graphite anodes was tried. They were satisfactory for periods up to two hours, but then became passive and plating deteriorated. Use of graphite anodes is not recommended.

Parts to be plated (cathodes) were weighed, cleaned, activated, dried, and re-weighed before going to the furnace. They were pre-heated to the same temperature as the melt before immersion. After plating, parts were cooled in an empty mullite crucible under an argon atmosphere. After reaching room temperature, they were washed in a solution of water and alkaline detergent to

remove excess cyanide which was collected for destruction by calcium hypochlorite treatment. The parts were then weighed and inspected. It should also be noted that an inert gas was used to blanket the cyanide bath at all times when molten. Initially, a blanket of nitrogen was used, but a change was made to argon to assure that nitrogen could not be absorbed in substrates or deposits which might be detrimental.

Since high temperatures and potentially corrosive conditions were in existence in the fused salt baths, a complete revision of the test specimens was necessary. Teflon can not withstand the temperatures involved, so fixturing was another problem that had to be addressed. Initial specimen fixtures were made of stainless steel. Drilled and tapped rod samples could be suspended on a threaded stainless shaft. Unthreaded rods or rectangular plates could be suspended from stainless fixtures with adjustable fingers. These were satisfactory for but a short time. Scaling and erosion developed which became suspect as sources of deposit contamination and blistering. The next family of fixtures were all nickel plated. This resisted deterioration for a longer period of use; however erosion eventually developed - possibly due to pinholes or porosity in the coating. The third stage of fixture development consisted of nickel plating and platinum plating the stainless steel. This was the most satisfactory modification; it could be cleaned and replated as required.

Table XVI provides plating parameters and test data for a series of specimens of various refractory metals and alloys on which iridium was deposited from the fused salt bath. In all cases, the sample plating started with conventional direct current deposition. Iridium concentrations were based on calculated values from anode and cathode weight differences. Figure 31 shows some calculated plating efficiencies for iridium deposited on rotating rod stock based on calculated iridium concentration of the bath. It is impossible to plot a reliable trend line for efficiency based on iridium content. The data points are so scattered that it can only be concluded that plating efficiency is dependent on some factor other than iridium concentration alone. A comparison of these efficiencies with those reported by Withers and Ritt is hindered by the fact that they had anode to cathode ratios of 4:1 while higher ratios of 20:1, or more, were prevalent in this study.

It was observed that iridium of better surface appearance was obtained when a peak current density of  $3.225 \text{ Amp/dm}^2$  (30 ASF) was used and a pulse of 90 milliseconds "on" time and 30 milliseconds "off" time was employed. The iridium melt had a characteristic orange color when properly functioning. A change in color to a yellowish shade indicated an out-of-range iridium condition for good deposits. The difficulties in obtaining good deposition rates when iridium concentration was high might indicate that the

TABLE XVI - MOLTEN SALT IRIIDIUM PLATING EFFICIENCY STUDY

FUSED SALT IRIIDIUM EFFICIENCY STUDIES												
SPECIMEN NUMBER	SPECIMEN DESCRPT.	FORWARD PULSE		PEAK FORWARD CUR. DENS. (Amp/Dm <sup>2</sup> )	CALCULATED AVERAGE CUR. DENS. (Amp/Dm <sup>2</sup> )	TIME PLATED WITH DC (Hours)	TIME PLATED WITH PULSE (Hours)	IRIDIUM CONCENT. (G/L)	SPEED (RPM)	ACTUAL COATING THICKNESS (in)	THEORET. COATING THICKNESS (in)	CALCULATED PLATING EFFICIENCY %
		ON/OFF (Milli sec)	DC Only									
Ir 01	Ta-10W Rod 0.375" Dia		DC Only	3.225	3.225	3.00	0.00	15	30	0.0022	0.0041	54.0
Ir 02	Molyb Rod 0.5" Dia.		DC Only	3.225	3.225	3.27	0.00	20	60	0.0019	0.0044	42.7
Ir 03	Cb 103 Rod 0.5" Dia.		DC Start ?/?	3.225 ?/?	3.225 3.225	0.52	2.88	14 14	60 60	0.0032	0.0046	69.2
Ir 04	Ta-10W Rod 0.375" Dia		DC Start 8.0/2.0	2.688 3.360	2.688 2.698	0.33	2.67	10 10	80 80	0.0023	0.0034	67.7
Ir 05	Tung. Rod 0.25" Dia.		DC Only	3.225	3.225	4.22	0.00	11 11	80	0.0020	0.0057	34.9
Ir 06	Tung. Foil		DC Start 90.0/30.0	3.225 4.300	3.225 3.225	0.08	5.83	11 11	Vert. Recip @ 12 RPM	0.0019	0.0080	23.7
Ir 07	Tung. Foil		DC Start 90.0/30.0	3.225 4.300	3.225 3.225	0.33	2.83	11 11	Vert. Recip @ 12 RPM	0.0011	0.0043	25.6
Ir 08	Rhenium Rod 0.5" Dia.		DC Start 90.0/30.0	3.225 4.300	3.225 3.225	0.22	2.35	9 9	30 30	0.00003	0.0035	0.9

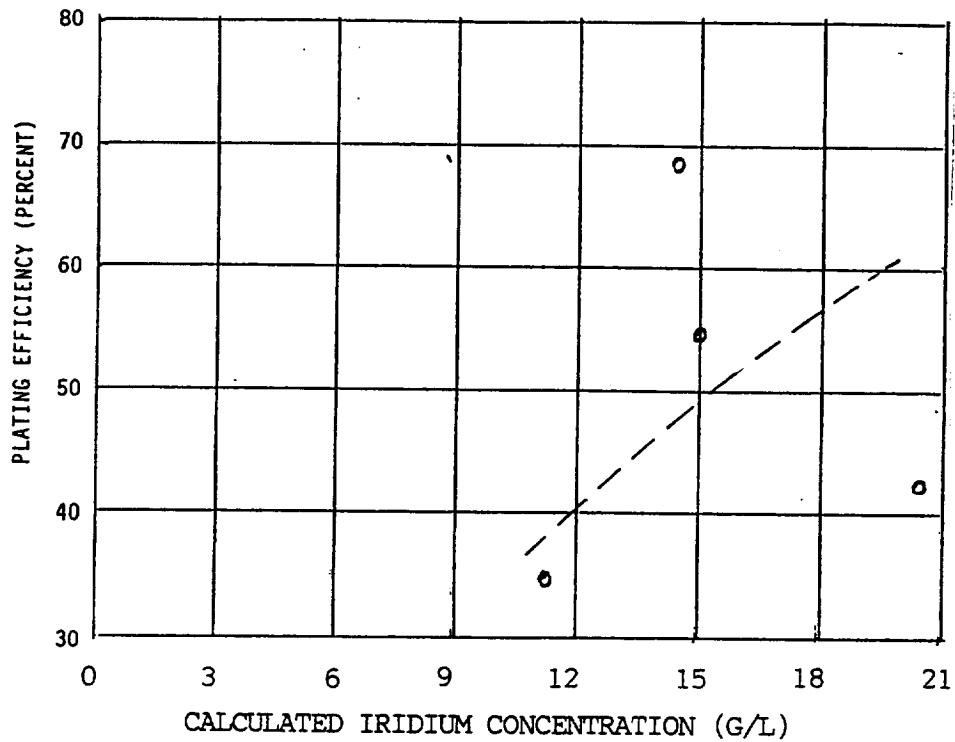


Figure 31. Calculated Plating Efficiencies for Iridium Deposited From Fused Salt Baths on Rotated Rods of Various Refractory Metals.

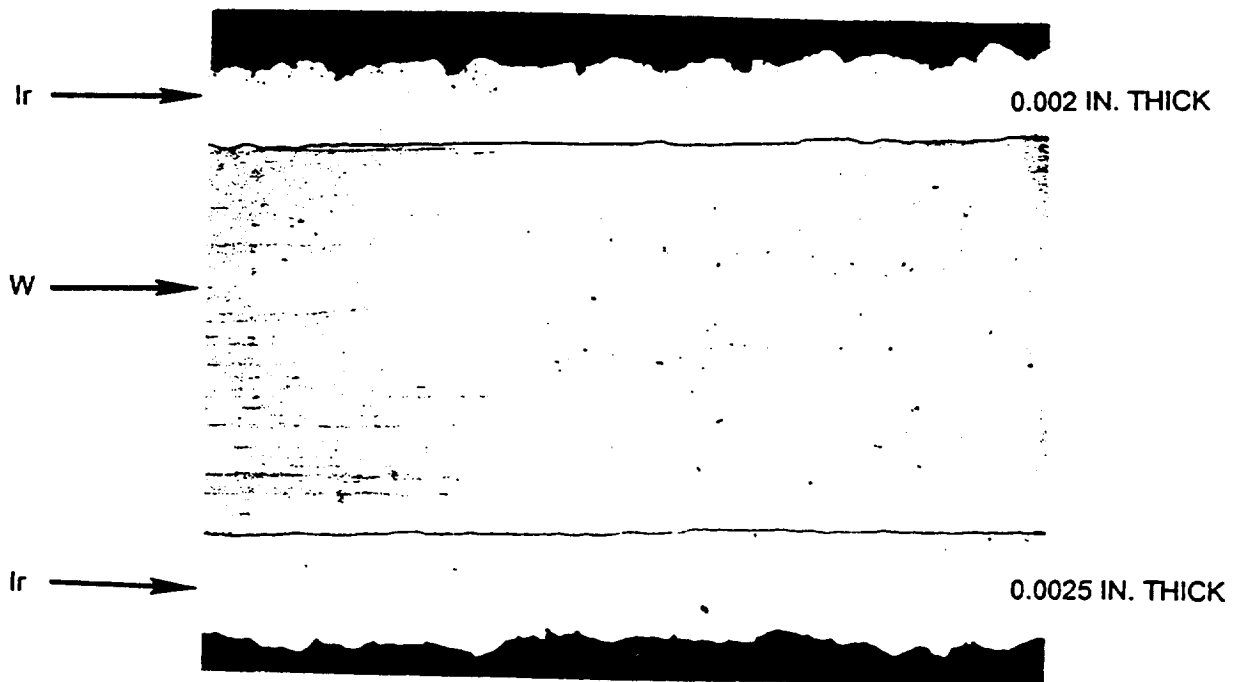
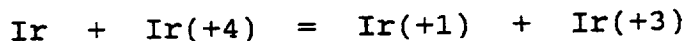


Figure 32. Photomicrograph of Iridium Deposited on a Tungsten Foil From a Fused Salt Bath. Magnification 200X, Unetched. Photo Was Furnished by TRW, Inc.

iridium is complexed in a manner not favorable for deposition. A reason for this could be the use of very small anode areas in relation to cathode areas. Under these conditions, the anode current density is extremely high, and oxidation of iridium to a higher valence such as Ir(+4) may occur. It would be expected that this situation would be remedied by exposure of the melt to iridium metal when the bath is idle:



However, rate reactions enter the picture and continued plating at unfavorable anode-cathode area ratios restores poor efficiencies to the bath. A study was made to determine if use of auxiliary anodes of another metal might support continued use of baths with poor plating efficiencies. Selection of such anode material was based on a need for a high temperature metal which would not be chemically attacked by the melt and would pass a substantial part of the total anodic current. Pure rhenium anodes were made from stock supplied by Rhenium Alloys, Inc. (formerly Sandvik). Trials using this material have shown that bath life can be improved, no corrosive attack is apparent, and no rhenium is codeposited with iridium coatings (the latter was confirmed by Pratt & Whitney in a chemical analysis of iridium plated on Mo-47Re).

Figure 32 shows a cross-section of a tungsten foil plated with iridium from the fused salt electrolyte. The coating is somewhat rough, but the coherency looks good and no voids or other defects are noted.

#### Rhenium - State of the Art

Brenner [27] suggested that the deposition potential of rhenium should make it easy to plate in alkaline or acidic aqueous solutions. However, the process proceeds at a low plating efficiency of about ten percent. He described the preferred plating bath to be an acid sulfate solution containing 11 g/l potassium per-rhenate,  $\text{KReO}_4$ , and a pH of about 1. Deposits were generally hard, brittle, and stressed. Camp [28] had better success with deposition of a hard, corrosion-resistant rhenium from a slightly acid, phosphate complexed bath - deposits to 50  $\mu\text{m}$  (0.002 in) in thickness could be obtained without intermediate stress relieving treatments.

Hosokawa [29] reported benefits in use of pulsed current to plate rhenium with fewer cracks in deposits of up to 2  $\mu\text{m}$  (0.00008 in). Puipe [30] divided rhenium baths investigated into two groups: (1) those with best plating efficiency (sulfate type), and (2) those with best deposit quality (phosphate or oxalate types). He noted that the sulfate bath current efficiency was only 5 to 7 percent at room temperature using a current density of 10  $\text{amp}/\text{dm}^2$  (92 ASF). Both processes produced deposits showing cracks when



heated to about 1000°C. He examined pulsed current parameters and found that extremely short pulses having very high peak current densities resulted in crack-free rhenium after exposure to high temperatures.

Safranek [31] stated that early rhenium plating baths produced deposits that were hard and brittle. It was believed that rhenium was deposited as the hydride which was unstable in air and moisture. Heating the deposit to 1000°C in hydrogen for about fifteen minutes produced tarnish-resistant metal. Safranek mentions that the maximum thickness of quality rhenium coatings was reported to be 2  $\mu\text{m}$  when deposited from a solution containing 12 g/l potassium perrhenate, 30 g/l sulfuric acid, and 50 g/l ammonium sulfate at room temperature and 20 amp/dm<sup>2</sup> (195 ASF).

Meyer [32] reported rhenium deposited from sulfamic acid solutions was improved by the addition of magnesium sulfamate and aluminum compounds to reduce internal stress to permit deposition of thicker coatings at higher current densities. Deposits were made between 60° and 80°C, 10 to 15 amp/dm<sup>2</sup>, with moderate agitation in a solution containing 10 g/l potassium perrhenate, 10 g/l sulfuric acid (to lower pH to 1 to 1.5 for brighter deposits with increased plating efficiency), 25 g/l ammonium sulfate (to increase conductivity and efficiency - especially at low current density), and 30 g/l of magnesium sulfamate to reduce stress.

Camp [28] investigated the differences in deposits from sulfuric acid, citric acid, citrate, and phosphate baths. Those from the sulfate bath darkened quickly. Those from citric acid and citrate baths remained bright for 4 to 7 months, and deposits from slightly acid phosphate baths remained bright for more than a year. Ivanova, et al, [33] examined rhenium solutions containing fluorides. At current densities of 5 to 15 amp/dm<sup>2</sup> and temperatures of 30 to 50°C, these deposits were fine-grained and hexagonal-close-packed (HCP) lattice structure.

Kaplan and Tuffias [34] described fabrication of a rhenium thrust chamber based on a design by NASA-JPL. Chemical vapor deposition (CVD) of the structure was performed by passing rhenium pentachloride over a graphite mandrel at 1100° to 1400°C where pyrolytic reduction occurred to produce rhenium metal and chlorine gas.

#### **Rhenium Plating Efficiency Studies**

Five different rhenium electrolytes were investigated as potentially viable commercial processes for high-temperature coatings. Of these, four were aqueous in nature while one was based on a fused salt formulation. The fused salt evaluation was actually performed on a separate contract for NASA-Lewis Research Center, but it is appropriate to mention the effort since exploration of this process has not been reported in the literature.

The fused salt rhenium bath was prepared by blending 820 grams of alkali cyanides consisting of 70 % sodium and 30 % potassium cyanide salts as a low melting eutectic. These were melted in a Mellen top loading furnace of a type previously described. The final melt had a volume of 547 ml within a 750 ml Coors alumina crucible. The molten cyanide was charged with rhenium by two simultaneous techniques. Two rhenium anodes were partially submerged in the melt and were partially dissolved by passing about 300 amperes per square foot of alternating current between them. 5.4 grams of finely divided rhenium powder, supplied by Rhenium Alloys, Inc., were added to the melt for possible chemical dissolution. After 124 hours, 5.4 grams of the rhenium anodes had dissolved. About two weeks were required for the finely divided rhenium powder to dissolve.

The first test specimen was a Ta-10W rod that was plated when the rhenium concentration had only reached 1 g/l. No deposit was found after 3 hours of plating at  $3.66 \text{ A/dm}^2$  (34 ASF). A Cb103 rod was plated at  $3.01 \text{ A/dm}^2$  (28 ASF) when the rhenium concentration reached 20 g/l. No rhenium deposition was evident. A Mo-47 Re alloy strip was then plated at  $0.54 \text{ A/dm}^2$  (5 ASF) for 2 hours, and a slight weight gain was measured. The bath rhenium was increased to 45 g/l and a second Mo-47Re strip plated at  $1.62 \text{ A/dm}^2$  (15 ASF) for 2 hours. A slight weight gain of 3.2 mg was recorded. At this rate it would take 520 hours to plate 25  $\mu\text{m}$  (1 mil) of rhenium. The process was abandoned.

The first aqueous rhenium electrolyte studied was the acid sulfate bath composed of 5 g/l rhenium (from potassium perrhenate) and 5 ml/l of sulfuric acid. Various operating temperatures ranging from 20° to 80°C were used, although some of the higher temperatures were not by intent. The aqueous rhenium baths must be operated at extremely high current densities to produce crack-free deposits of sufficient purity to resist tarnishing and deterioration. These high current densities produce extensive heat in the electrolyte which is not easily dissipated in small baths. The current densities are often sufficiently great so as to heat the cathode supporting shaft to a point where the solution starts to boil locally. It was necessary to add a large volume water jacket around the electrolyte container and, in some cases, add ice to the water jacket to keep temperature under control.

Table XVII provides specimen information, plating parameters, and sample appearance for plating runs conducted in the acid rhenium sulfate bath. It will be noted that plating efficiencies are very low, in line with the values reported in the literature. It was noted that increasing the bath temperature and the rhenium content generally led to slightly better plating efficiencies. A good plating efficiency did not necessarily result in good plate quality. The appearance of the rhenium deposits from this bath degraded very rapidly with exposure to the laboratory atmosphere.

TABLE XVII - AQUEOUS RHENIUM SULFATE BATH PLATING EFFICIENCY STUDY

ACID RHENIUM SULFATE BATH PLATING EFFICIENCY STUDIES (4-5 G/L RHENIUM, 5 ML/L SULFURIC ACID)													
PLATING RUN NO.	DIRECTION	TIME	FORWARD PULSE	REVERSE PULSE	PEAK FORWARD CUR. DENS (Amp/Dm <sup>2</sup> )	PEAK REVERSE CUR. DENS (Amp/Dm <sup>2</sup> )	AVE. FWD. CUR. DENS (Amp/Dm <sup>2</sup> )	CALCULATED PLATING TIME (Hours)	BATH TEMP. (°C)	DEPOSIT WEIGHT (Grams)	WEIGHT AT 100% EFF. (Grams)	TOTAL CYCLE	PLATING EFF. (%)
Re 01 (09)	FWD/REV (Milli sec)	1.0/1.0	FWD. ONLY	ONLY	95.668	0.000	47.834	0.50	20-45°C	0.3663	4.8156	7.61	
Edges of Re 01 appeared bright metallic; center was dark gray.													
Re 02 (10)	FWD. ONLY	0.03/0.27	FWD. ONLY	ONLY	93.696	0.000	9.369	0.50	25-29°C	0.0281	0.9433	2.98	
Edges of Re 02 appeared bright metallic; center was dark gray.													
Re 03 (11)	FWD. ONLY	0.1/0.9	FWD. ONLY	ONLY	123.284	0.000	12.328	0.50	40-49°C	0.0700	1.2411	5.64	
Re 03 appeared gray colored with majority of surface rough and dark.													
Re 04 (12)	FWD. ONLY	0.5/4.5	FWD. ONLY	ONLY	135.613	0.000	13.561	0.50	44-48°C	0.1110	1.3652	8.13	
Re 04 appeared good at edges, but black streaks were in central portion.													
Re 05 (14)	FWD. ONLY	1.0/10.0	FWD. ONLY	ONLY	146.462	0.000	13.315	0.50	45-48°C	0.1154	1.3404	8.61	
Re 05 edges appeared good; some black spots in central portion.													
Re 06 (15)	FWD. ONLY	1.0/11.5	FWD. ONLY	ONLY	138.571	0.000	11.086	0.50	39-44°C	0.1204	1.1170	10.78	
Re 06 edges looked very good; central portion was darker in color.													
Re 07 (16)	FWD. ONLY	1.0/10.0	FWD. ONLY	ONLY	151.886	0.000	13.808	0.50	60-63°C	0.2460	1.3901	17.70	
Re 07 had uniform metallic luster over polished gold substrate.													
Re 08 (21)	FWD. ONLY	1.0/10.0	FWD. ONLY	ONLY	168.160	0.000	15.287	0.50	80-83°C	0.3440	1.5390	22.35	
Re 08 had chemically attacked edges and cracks over much of surface.													
Re 09 (22)	FWD. ONLY	DC ONLY	FWD. ONLY	ONLY	49.314	0.000	49.314	0.50	50-70°C	0.4563	4.9645	9.19	
Re 09 was light gray with dark edges and rough surface.													
Re 10 (23)	44/11	1.0/10.0	1.0/10.0	274.184	24.926	0.50	66-74°C	0.2884	2.5093	11.49			
Re 10 was a uniform matte gray in appearance.													
Re 11 (24)	77/27	1.0/10.0	0.75/8.25	141.037	0.740	12.822	0.50	50-51°C	0.0648	1.2908	5.02		
Re 11 had satisfactory edges, but remainder had black rotational line streaks.													
Re 12 (25)	33/11	1.0/10.0	1.0/10.0	352.593	352.593	32.054	0.50	51-61°C	0.4944	3.2269	15.32		
Re 12 had a bright uniform appearance with good luster; rhenium at 6.5 g/l.													
Re 13 (26)	33/11	1.0/10.0	1.0/10.0	352.593	352.593	32.054	1.00	51-61°C	0.9270	6.4539	14.36		
Re 13 had a dull gray surface with striations, bumps, and pits; rhenium at 7.4 g/l.													
Re 14 (27)	33/11	1.0/10.0	1.0/10.0	492.643	24.657	44.786	7.00	51-56°C	4.8238	63.1212	7.64		
Run 2	33/22	1.0/10.0	1.0/10.0	492.643	14.794	44.786	4.00	51-61°C	1.6328	36.0693	4.53		
Run 3	33/11	1.0/10.0	1.0/10.0	492.643	48.821	44.786	7.00	50-56°C	4.1265	63.1212	6.54		
Re 14 was plated to an average thickness of 0.0097 in.; color was a uniform dark gray; rhenium at 9.7 g/l.													
Re 15 (28)	33/55	1.0/10.0	1.0/10.0	165.694	0.493	15.063	0.50	37-47°C	0.1806	1.5164	11.91		
Re 15 had a uniform, smooth light gray matte appearance.													
Re 16 (29)	300/600	1.0/99.0	1.0/99.0	197.255	197.255	1.973	0.50	47-51°C	0.0216	0.1986	10.88		
Re 16 was smooth surfaced and dark gray; little hydrogen during plating.													
Re 17 (30)	33/99	1.0/10.0	1.0/10.0	108.490	108.490	9.863	0.50	52-61°C	0.0949	0.9929	9.56		
Re 17 had a dark gray smooth surface with striations; little hydrogen during plating.													
Re 18 (17)	33/11	1.0/10.0	1.0/10.0	347.168	347.168	31.561	0.50	51-60°C	0.3417	3.1773	10.75		
Re 18 had a bright, uniform deposit; plated over polished gold.													
Re 19 (28)	33/55	1.0/10.0	1.0/10.0	168.160	168.160	15.287	0.50	49-52°C	0.1637	1.5390	10.64		
Re 19 appeared light gray with a smooth matte metallic look.													
Re 20 (28)	33/66	1.0/10.0	1.0/10.0	141.037	141.037	12.822	0.50	46-54°C	0.1112	1.2908	8.62		
Re 20 was light gray in color with some microroughness.													
Re 21 (28)	33/55	1.0/10.0	1.0/10.0	168.160	168.160	15.287	0.50	54-61°C	0.1495	1.5390	9.71		
Re 21 had a uniform metallic luster; surface had microroughness.													



It was necessary to put these samples in a dessicator to decrease the deterioration rate. It will be noted that rhenium plating efficiencies were calculated for the total plating cycle, and any periodic reverse current was considered a part of the forward cycle from a time standpoint. This was based on the fact that rhenium metal deposits on the cathode acted as an inert anode during the reversal part of the cycle and were considered to not dissolve. Some plating of the platinized titanium or columbium mesh anodes may have occurred during these reversals. This convention was followed though all of the rhenium studies.

The next bath examined was the phosphate complexed solution. The electrolyte was composed of 10 g/l rhenium (from potassium perrhenate), 80 ml/l of ammonium hydroxide, and 200 g/l of phosphoric acid. Investigation was conducted over a bath temperature range of 56° to 77°C and average current densities of about 5.5 to 129 amp/dm<sup>2</sup>. Deposition data, sample descriptions, and calculated plating efficiencies are shown in Table XVIII. Rhenium plating efficiencies were not graphically compared in this study due to the relatively narrow range of efficiencies encountered.

After one year, the deposits with best appearances were Specimens 37, 38, 39, 40, and 41 (although 41 exhibited peeling). All of these specimens were deposited using pulsed current with a high peak current density. Figure 33 shows the specimens plated with rhenium from the phosphate bath in this study.

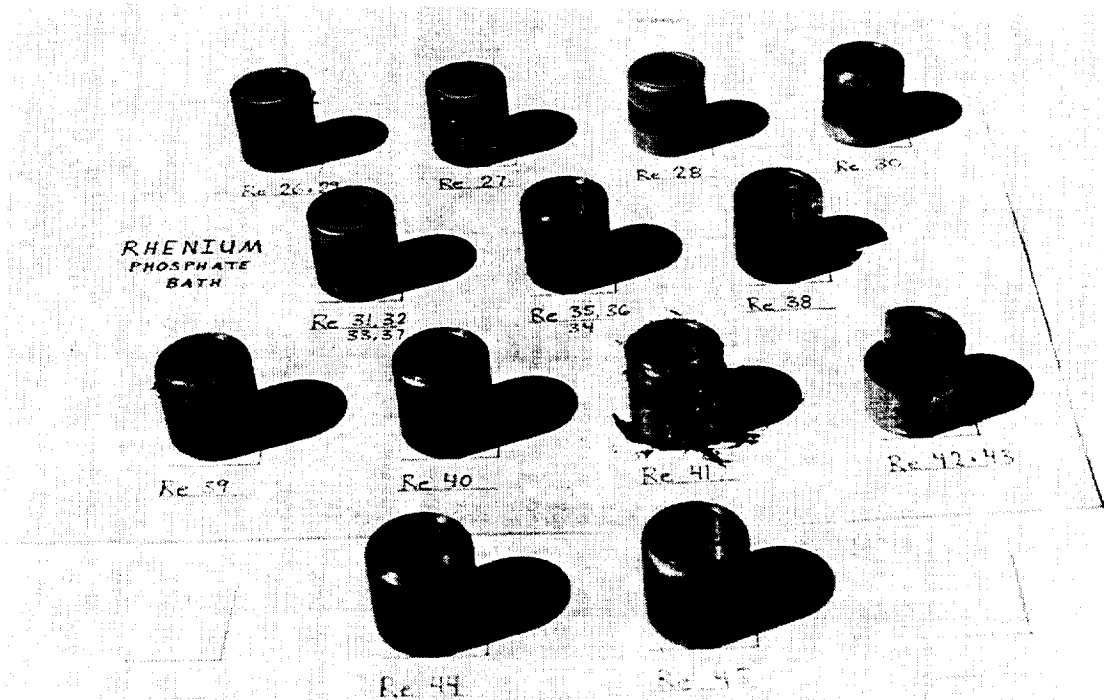


Figure 33. Rhenium Phosphate Deposits After One Year Exposure.

TABLE XVIII - AQUEOUS RHENIUM PHOSPHATE BATH PLATING EFFICIENCY STUDY

RHENIUM PHOSPHATE BATH PLATING EFFICIENCY STUDIES (10 G/L RHENIUM, 80 ML/L AMMONIUM HYDROXIDE, 200 G/L PHOSPHATE)													
PLATING RUN NO.	DIRECTION	TIME	FORWARD PULSE	REVERSE PULSE	PEAK FORWARD	PEAK REVERSE	CALCULATED AVE. FWD. CUR. DENS.	PLATING TIME (Hours)	BATH TEMP. (°C)	DEPOSIT WEIGHT (Grams)	EFFICIENCY AT 100% (Grams)	WEIGHT	TOTAL CYCLE
(CYLINDER NUMBER)	FWD/REV	(MilliSec)	ON/OFF (MilliSec)	ON/OFF (MilliSec)	(Amp/Dm)	(Amp/Dm)	(Amp/Dm)	(Hours)	(°C)	(Grams)	(Grams)		
Re 26 (33)	FWD. ONLY	1.0/10.0	FWD. ONLY	295.882	0.000	26.898	0.50	60-71°C	0.1028	2.7081	3.80		
	Re 26 had a moderate gray color of neutral brightness.												
Re 27 (34)	FWD. ONLY	1.0/1.0	FWD. ONLY	99.614	0.000	49.807	0.33	57-64°C	0.0658	3.3093	1.99		
	Re 27 had a moderate gray color of neutral brightness.												
Re 28 (35)	FWD. ONLY	DC ONLY	FWD. ONLY	88.765	0.000	88.765	0.10	60-77°C	0.0234	1.7872	1.31		
	Re 28 had a moderate luster and neutral gray color.												
Re 29 (33)	FWD. ONLY	1.0/3.0	FWD. ONLY	266.294	0.000	66.573	0.10	60-67°C	0.0263	1.3404	1.96		
	Re 29 had a moderate luster and neutral gray color.												
Re 30 (36)	FWD. ONLY	0.1/0.9	FWD. ONLY	216.980	0.000	21.698	0.50	58-61°C	0.0557	2.1844	2.55		
	Re 30 had a smooth and lustrous gray appearance.												
Re 31 (37)	FWD. ONLY	3.0/33.0	FWD. ONLY	82.847	0.000	6.904	0.50	58-61°C	0.0246	0.6950	3.54		
	Re 31 had a shiny, smooth, bright appearance; plated over polished substrate.												
Re 32 (37)	FWD. ONLY	3.0/57.0	FWD. ONLY	182.461	0.000	9.123	0.50	58-60°C	0.0263	0.9184	2.86		
	Re 32 had a shiny, smooth, bright appearance; plated over polished substrate.												
Re 33 (37)	FWD. ONLY	2.0/99.0	FWD. ONLY	274.184	0.000	5.429	0.50	56-60°C	0.0146	0.5466	2.67		
	Re 33 had a shiny, smooth, bright appearance; plated over polished substrate.												
Re 34 (38)	FWD. ONLY	0.3/0.1	FWD. ONLY	26.136	0.000	19.602	0.50	60-61°C	0.0136	1.9734	0.69		
	Re 34 appeared bright metallic gray with surface smooth and lustrous; plated over polished gold.												
Re 35 (38)	FWD. ONLY	3.0/87.0	FWD. ONLY	295.882	0.000	9.863	0.50	60-63°C	0.0341	0.9929	3.43		
	Re 35 appeared gray colored and smooth over gold.												
Re 36 (38)	3/5	0.3/2.7	2.0/3.0	98.627	98.627	9.863	0.50	58-60°C	0.0364	0.9929	3.67		
	Re 36 appeared to duplicate smooth and rough areas of Re 35.												
Re 37 (37)	FWD. ONLY	3.0/57.0	FWD. ONLY	271.225	0.000	13.561	1.00	58-60°C	0.0617	2.7305	2.26		
	Re 37 appeared bright, smooth, and shiny gray; sample has accumulated 0.1277 g of rhenium.												
Re 38 (39)	FWD. ONLY	3.0/60.0	FWD. ONLY	269.253	0.000	12.822	0.50	60-65°C	0.0349	1.2908	2.70		
	Re 38 appeared bright, smooth, and shiny.												
Re 39 (40)	FWD. ONLY	3.0/12.0	FWD. ONLY	246.568	0.000	49.314	0.50	60-66°C	0.1152	4.9645	2.32		
	Re 39 had the best appearance of all specimens plated.												
Re 40 (41)	FWD. ONLY	2.0/3.0	FWD. ONLY	234.240	0.000	93.696	0.50	60-69°C	0.2203	9.4326	2.34		
	Re 40 had a cloudy appearance.												
Re 41 (42)	FWD. ONLY	3.0/2.0	FWD. ONLY	205.638	0.000	123.383	0.25	58-72°C	0.1280	6.2106	2.06		
	Re 41 appeared comparable to Re 39.												
Re 42 (43)	FWD. ONLY	3.0/2.0	FWD. ONLY	98.627	0.000	59.176	0.50	60-62°C	0.0794	5.9574	1.33		
	Re 42 appeared gray in color; shiny towards center and duller at edges.												
Re 43 (43)	FWD. ONLY	3.0/2.0	FWD. ONLY	214.514	0.000	128.709	0.33	58-72°C	0.1379	8.5518	1.61		
	Re 43 had a gray metallic appearance with uniform color and fine texture.												
Re 44 (44)	2/1	0.3/0.1	0.1/0.9	96.655	96.655	22.305	0.50	61-69°C	0.1289	2.2455	5.74		
	Re 44 appeared gray metallic with duller areas at edges.												
Re 45 (20)	FWD. ONLY	3.0/33.0	FWD. ONLY	295.882	0.000	24.657	1.20	60-64°C	0.0866	5.9574	1.45		
	Re 45 was light gray with darker bands at edges and some small blisters in one area.												

Figure 34 shows a cross-section of the coating on Specimen No. 39 which was deposited using a 25 percent pulse duty cycle and peak current density of  $246 \text{ A/dm}^2$  (2260 ASF). Figure 35 shows a view of Specimen No. 43 plated with a 60 percent duty cycle and a peak current density of  $215 \text{ A/dm}^2$  (1980 ASF). The former deposit has

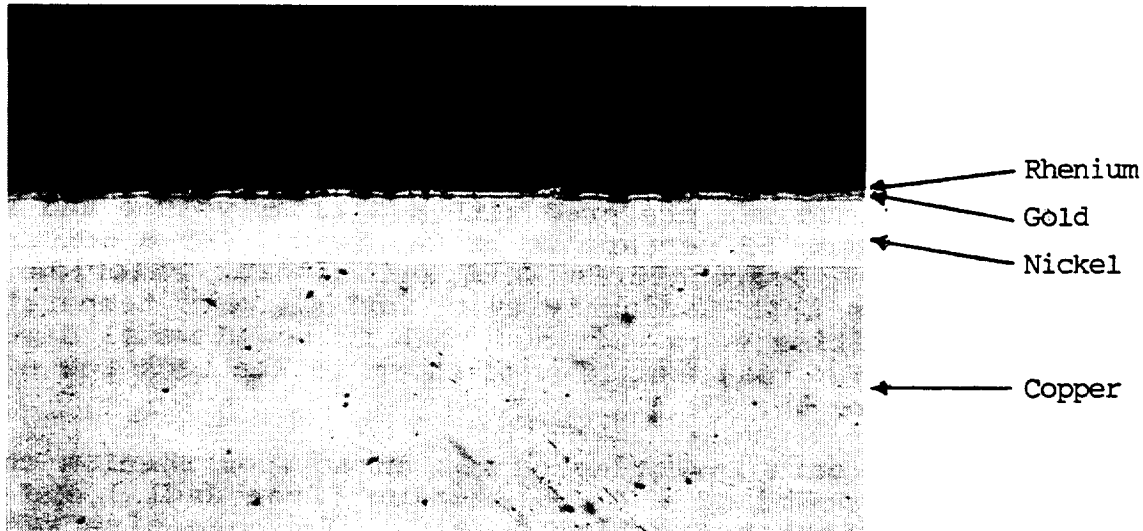


Figure 34. Metallographic Section of Specimen No. Re 39 Showing Discontinuities in Rhenium Coating. Magnification 200X.



Figure 35. Metallographic Section of Specimen No. Re 43 Showing A More Continuous Rhenium Coating. Magnification 200X.

numerous voids which may be pores and/or cracks which are not evident in the coating of the latter specimen. Although both samples were plated with extremely high peak current densities, the duty cycles were quite different. The better coating continuity sample was plated with a duty cycle in excess of 50 percent, but

the duty cycle was 25 percent for the discontinuous coating. The pulse "off" time for both samples was 2 milliseconds. Since co-deposited hydrates are suspected to be a contributor to poor corrosion performance in aqueous rhenium deposits, it is reasonable to postulate a greater entrapment of such hydrates from shorter peak "on" times in the lower duty cycles. This may be related to rhenium being in a septavalent (+7) state in a large complexed anion. The higher duty cycle provides time for more complete reduction of the perrhenate complex. This might explain why other investigators used hydrogen atmosphere heat treatments of rhenium deposits to enhance corrosion resistance performance.

A third rhenium bath was prepared with a 2 liter volume and evaluated using 26 grams of perrhenic oxide,  $\text{Re}_2\text{O}_7$ , for a concentration of 10 g/l. Hydrochloric acid and lithium chloride were added to increase bath conductivity. Various bath temperatures and current densities were examined, but no sound metal deposits could be obtained. Test samples are shown in the back row of the photograph, Figure 36.

The last rhenium bath investigated was an aqueous rhenium chloride solution composed of 6.4 g/l rhenium (from  $\text{ReCl}_5$ ) and 36.4 g/l of 37% by weight hydrochloric acid. The bath size was 0.5 liter. Table XIX summarizes data for test samples produced at various current densities and pulsing conditions.

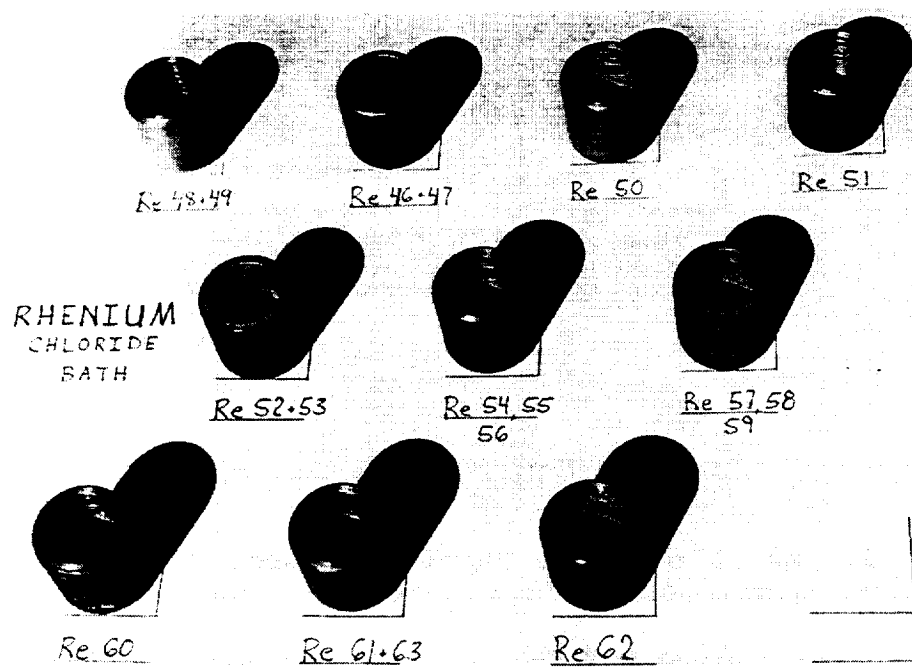


Figure 36. Perrhenic Oxide and Rhenium Chloride Bath Specimens.





Deposits from this bath exhibited potential for depositing thick rhenium; however, the deposits obtained were subject to rapid deterioration when exposed to the laboratory environment. A bath for rhenium plating is shown in Figure 37.



Figure 37. Rhenium Phosphate Complexed Plating Facility.

## Conclusions and Recommendations

### Ruthenium Plating

Ruthenium is easily plated from sulfamate or nitrosyl sulfamate complexed solutions. However, the deposits of useful thicknesses are highly brittle, stressed, and cracked. Combining these characteristics with the fact that ruthenium suffers greater rates of material recession at high temperature in oxidizing environments, this metal has far less useful potential than the other platinum group metals such as platinum, iridium, and rhodium for high temperature oxidation protection. In spite of these deficiencies, there is one application where ruthenium deposits may be of use, and that is in the application of intermediate high temperature films between molten salt deposits and diffusion resistant substrates of refractory metals and alloys.

An example of such an application might be found in fused salt iridium coating of tungsten, rhenium, or rhenium alloys of molybdenum or tungsten. These substrates are moderate to very strong

diffusion barriers. Direct deposition of iridium on these metals is desired because of the high melting temperatures afforded by these combinations and the good oxidation protection of iridium. A key ingredient to the success of such combinations is the ability to produce high integrity bonds to the substrate. Best bond preparation of most of these substrates involves aqueous processing with an initial electrodeposit (usually called a strike) that affords an interface free of oxides and voids. This activation of the substrate must be retained for the period of time required to coat the surface with a protective electrodeposit. The time of "activeness" of this surface is usually dependent on producing a short lived hydride layer on the substrate, or on stabilizing the surface from oxidation by an aqueous film of very low pH in which oxides of the substrate are not promoted.

Iridium, from a fused salt bath, can not be used as a strike on these substrates because of the aqueous activation film which would contaminate and destroy the melt. Rhodium can be plated as a strike on many of such substrates with good adhesion obtained. Rhodium might provide a good interface bonding layer for many applications; however, ruthenium might be more appropriate as the service temperature is increased - this being due to the higher melting temperature of ruthenium (2400°C) as opposed to rhodium (1960°C). The ruthenium layer would be very thin to minimize any microcracking; diffusing the ruthenium interface with the substrate and iridium outer coating (at 2100° to 2200°C) would circumvent any potential problems from the microcracking.

### Iridium Plating

Successful iridium plating was only achieved in the fused cyanide salt bath at melt temperatures of 600° to 650°C and moderate to low current densities. The plating rate is slow since the bath can not be rapidly agitated. The expense of iridium as an anode makes anode cathode ratios very unfavorable for high speed plating; however, a significant development was made in this program to increase anode area by the use of rhenium anodes in array with iridium.

Fixturing is a major concern in fused salt iridium plating due to the high melt temperature. Electrical contact points had to be alternated frequently to assure that all cathode (workpiece) surfaces were adequately coated. Stainless steel fixturing degraded with time and required coating with electrodeposited nickel. The use of platinum plating over the nickel prolonged fixturing life. Shielding to direct current to preferred areas of plating was another problem. Anode placement did not solve this because of the high throwing power (ability to plate into recessed areas) of the bath. In later work it was found that alumina tube stock and crucible cut-offs could be used as general shielding to redirect

current to desired locations.

Roughness of the substrate must be minimized to prevent thick deposits of iridium from becoming nodular. Fine grain structure and deposit smoothness are best achieved by depositing iridium in multiple layers with sanding or burnishing between layers. Preheating the part to be plated is essential to assure that the part is dry and to prevent chilling the melt in the vicinity of the part when initially submerged in the bath. Selection of an optimum current density and iridium concentration is not simple due to the fact that the iridium may exist in more than one complex or valence. It appears that iridium plates best from a very specific valence and complex state. This is in agreement with the conclusions reached by Withers and Ritt.

Heat treatment of specimens after the initial bonding strike and a thin (2.5 to 5  $\mu\text{m}$ ) iridium plate have been applied is recommended. This treatment should be in a hydrogen atmosphere and at at least 1200° to 1300°C to assure that no hydrated salts are present which might lead to blistering or delamination at high temperatures once the entire coating is applied.

Maintaining the fused salt bath composition is important. This requires careful measurement of anode and cathode weight changes. Since this will not account for proportionalization of iridium by valence or type of complex, it is essential that iridium plating rate be determined after each run. This will dictate when compositional changes must be made.

#### Rhenium Plating

Ability to electroplate rhenium from aqueous solutions is desired as (1) a diffusion barrier interface for certain substrates where platinum group metal deposits result in Kirkendall effect (void formation) upon exposure to high temperatures, and (2) as a high temperature refractory metal for engineering structural electroforms such as uncooled thrustors for satellite guidance systems. Rhenium also has an unusually high melting point for a metal at 3170°C.

Attempts to plate rhenium from a cyanide fused salt bath failed to yield useful deposits. It was much easier to deposit rhenium from aqueous baths, of which the phosphate complexed perrhenate solution produced the best coatings. Rhenium is highly stressed, brittle, and microcracked under most plating conditions. Cracks can be minimized in low deposit thicknesses by plating with very high current densities such as can be achieved with pulsed current deposition. From this respect, rhenium plating (from a valence of +7) can be compared to chromium plating (from a +6 valence).

Since peak current densities, often in excess of 150 A/dm<sup>2</sup> (1400

ASF), are involved, there is great thermal energy evolved. This necessitates making the bath volume large with good solution circulation to assure reasonable temperature control. Further study of the chloride bath is warranted, since plating rhenium from a +3 valence should result in less heat generation and lower current densities. Use of special directional membranes for plating cell dividers might promote less contamination of the cathode surface layer and lead to a deposit containing less hydrated co-deposits. Use of an argon blanket over the plating cell is also recommended as a deterrent to rhenium ion oxidation products that might contaminate the deposit. Until rhenium plating development reaches a point where sound, corrosion-resistant rhenium metal in the as-deposited condition can be demonstrated, it is recommended that hydrogen heat treatment be performed to reduce codeposited hydrates and various rhenium oxides.

**TASK II - INVESTIGATION OF HIGH INTEGRITY BONDING AND DIRECT  
DEPOSITION PROCEDURES FOR PLATINUM GROUP METALS  
AND INTERFACIAL COATINGS  
PART A - DEPOSITION OF INTERFACIAL COATINGS**

**Background**

Refractory metals and alloys, and most other engineering metals, require special chemical preparation treatments to assure good adhesion of any subsequent electrodeposits. Many of these metals are naturally oxidized, even at room temperature, to provide self protection from continued corrosion. These oxides can be chemically removed, but the deoxidation is only temporary - unless a protective film of greater permanence can be applied and adequately bonded. Thin deposits of such coatings are usually referred to as "strikes" or "flash coatings". They are most often followed by a deposit of another metal having properties or characteristics being sought to combat the service environment to which the end item is to be exposed.

The "strike" or interfacial coating must have properties making it suitable for use in the total coating system. Gold is often used as a protective strike on which other metals are deposited. However, gold has a melting point too low to find application on substrates to be protected at 2000°C or higher. Some metals that were considered in the current program were chromium, platinum, rhodium, rhenium, and iridium. Selection of a proper interface layer depends on many factors such as:

- (1) Is diffusion of the interface layer into the substrate or final oxidation barrier coating required?
- (2) Is the melting point of the interface layer sufficient to withstand the service temperature expected in the part?
- (3) Can coherent deposits of the interface metal be deposited without degrading the substrate surface?
- (4) Does the interface layer undergo diffusion phenomena that results in structural defects such as Kirkendall effect?

**Chromium Interface Deposits**

Kvokova and Lainer [35] note that the high rate of gaseous corrosion of molybdenum is due to the volatilization of oxidation products which begins at about 700°C; this results in the surface being constantly laid bare and the destruction process cycles all over again. They state that protection from oxidation can only be provided by the application of protective surface coatings of which electrodeposited types deserve most attention because of their ease of producing. Choice of such coatings involves many

factors such as resistance to oxidation, thermal stability, ratio of the coefficients of thermal expansion, properties of the intermediate diffusion zone, and most important - good and reliable bonding of the coating to the base metal. Nickel might be considered, but it has a significantly different coefficient of expansion, molybdenum diffuses rapidly through it (creating possibly brittle intermetallic compounds), and the melting point is only 1455°C.

They considered chromium to be advantageous because of its coefficient of thermal expansion being closer to that of molybdenum and tungsten, the melting point is 1890°C, alloys formed at the interface are solid solutions, and copious amounts of hydrogen are generated during plating assuring that the substrate surface is activated for reliable bonding. Kvokova and Lainer established a process for application of chromium coatings. For molybdenum, surface treatment began with normal cleaning followed by dipping in a solution of 100 g/l K Fe(CN) and 100 g/l KOH for 5 to 10 minutes. They suggested that electrochemical treatment was more effective. Treatment of molybdenum was in 70% sulfuric acid at room temperature and a current density of 25 - 30 A/dm<sup>2</sup> for 3 - 5 minutes. For tungsten they used 10 to 15% NaOH at room temperature and 30 - 40 A/dm<sup>2</sup>. An alternate process they recommended for molybdenum or tungsten was using alternating current in 15% NaOH at room temperature for 3 - 5 minutes, 35 - 40 A/dm<sup>2</sup>, and a voltage of 15 to 20.

Chromium plating was conducted using either a standard electrolyte (CrO<sub>3</sub>, 250 g/l; H<sub>2</sub>SO<sub>4</sub>, 2.5 g/l) at a temperature of 70°C and a current density of 30 A/dm<sup>2</sup>, or an electrolyte having a higher chromic acid to sulfate ratio (CrO<sub>3</sub>, 250 g/l; H<sub>2</sub>SO<sub>4</sub>, 0.75 - 1.5 g/l) at room temperature and a current density of 30 A/dm<sup>2</sup>. With these conditions, a dull, ductile, and nearly nonporous deposit of chromium is obtained with good bonding.

Safranek and Schaer [36] used similar procedures for the oxidation protection of molybdenum. Their chromium was deposited from a bath containing 250 g/l chromic acid and 2.5 g/l sulfuric acid. Conventional chromium was plated at 32.6 A/dm<sup>2</sup> (300 ASF) and a bath temperature of 48.9°C (120°F), while low-contraction chromium was deposited at 81.5 A/dm<sup>2</sup> (750 ASF) and a bath temperature of 85°C (185°F). Another process for bonding to molybdenum was based on the following process [37]:

1. Anodic etch in 70% sulfuric acid at room temperature using 200 ASF for 30 seconds.
2. Rinse in deionized water to remove the blue oxide film of the previous etch step.
3. Dip in an alkaline solution such as Vitrokleen at 40 g/l.

4. Rinse in deionized water.
5. Dip in 10% by volume sulfuric acid (96%) and deionized water rinse.
6. Chromium strike plate at 120°F minimum using 150 ASF for 60 sec. The chromium bath composition is 244 g/l chromic acid and 2.44 g/l sulfuric acid with lead anodes.
7. Rinse with deionized water and plate with selected metal.

Another procedure [38] suggests activation of molybdenum by anodic etching in one of the following solutions:

- |                  |                     |
|------------------|---------------------|
| 1. Sulfuric acid | 118 oz/gal          |
| Phosphoric acid  | 96 oz/gal           |
| Current density  | 70-80 ASF           |
| Time             | 2-3 minutes         |
| Temperature      | Room                |
| 2. Chromic acid  | 3.4 oz/gal          |
| Sulfuric acid    | 3.4 oz/gal          |
| Current density  | 1 A/in <sup>2</sup> |
| Time             | 10-30 seconds       |
| Temperature      | 138°F               |

Treatment in one of the above solutions is followed by etching in the following:

- |                        |               |
|------------------------|---------------|
| Potassium ferricyanide | 40 oz/gal     |
| Potassium hydroxide    | 13 oz/gal     |
| Current density        | 100 ASF       |
| Time                   | 1-1.5 minutes |
| Temperature            | 185°F         |

This is immediately followed by a standard high chromium bath deposit.

Use of chromium interface deposits were investigated using 0.375 in diameter molybdenum tubes. Sample No. 1 was scraped after an activation and plating procedure for plating on tungsten showed failure on molybdenum. Sample No. 2 was cleaned in a chlorinated solvent, detergent cleaned and rinsed, ultrasonically cleaned and fixtured for chemical processing. The following procedure was used:

1. Etched anodically in 43 weight percent NaOH at 54.5°C and 20 A/dm<sup>2</sup> for 4 minutes and deionized water rinsed.
2. Immersed in 50% by vol. percent nitric acid for 10 seconds following the start of gassing. Rinsing followed.



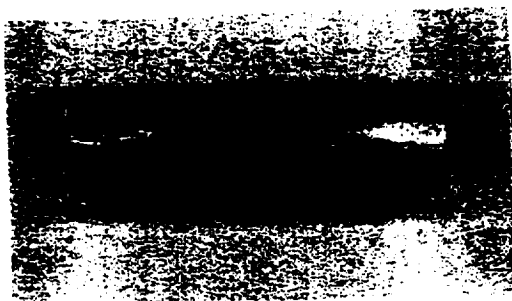
by volume HCl and rinsing.

4. Chromium striking was performed in a bath of the Safranek and Schaer recommended composition and 54.5°C using a current density of 20 A/dm<sup>2</sup> for 3 minutes followed by rinsing with deionized water.
5. The 6% HCl immersion, rinse, and chromium plating of Step 4 was repeated.
6. A Wood's nickel strike was applied for 3 minutes at about 3 A/dm<sup>2</sup> and followed with a nickel plate in nickel sulfamate solution.

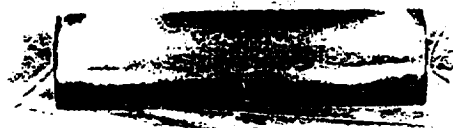
The nickel could not be peeled or dislodged from the sample, and the bond strength was considered good. Additional samples were processed and chromium plated in thicknesses of 12.5 and 25 μm to be evaluated for chromium adherence. These samples were processed as follows:

1. Clean in acetone, rinse in acetone, and air dry.
2. Ultrasonic clean anodically in Oakite 90 using 9.2 A/dm<sup>2</sup> for 3 minutes. Soak with ultrasonics on for 3 minutes, and warm rinse in water with ultrasonics applied.
3. Rinse for three more minutes in running water and immerse in a solution of 100 g/l KOH and 100 g/l K<sub>3</sub>Fe(CN)<sub>6</sub> at 60°C for 1 minute with agitation. Rinse.
4. Electropolish in 50 vol % sulfuric acid and 50 vol % H<sub>3</sub>PO<sub>4</sub> at 13 A/dm<sup>2</sup> for 10 minutes. Rinse for 1 to 2 minutes.<sup>3 4</sup>
5. Repeat Step 3 with rinsing, and cathodically activate the sample in concentrated (37%) HCl at 27.2 A/dm<sup>2</sup> (250 ASF) for 5 to 10 seconds.
6. Quickly immerse in a chromic acid solution predip to remove any chlorides before chromium plating.
7. Plate in the chromium bath at 81.5 A/dm<sup>2</sup> (750 ASF) for the required deposit thickness.

All specimens thus plated passed tape testing to determine if any poor adhesion existed. No chromium removal was noted. Some of the samples were vacuum heat treated at 1093°C (2000°F) and were found to exhibit satisfactory bonds, Figures 38 and 39. Specimens plated with 25 μm (0.001 In) of chromium appeared to be less porous and more resistant to tarnishing than those plated with 12.5 μm (0.0005 In) of metal.

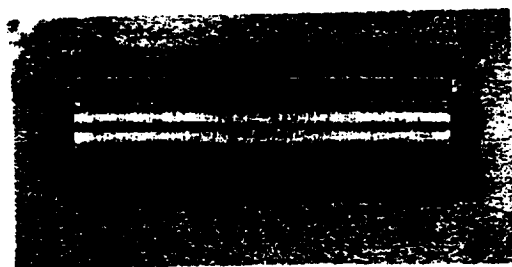


Specimen C06 - As Deposited



Specimen C07 - Heat Treated

Figure 38. Molybdenum Tube Specimens Plated With 25  $\mu\text{m}$  (0.001 In) of Chromium.



Specimen C10 - As Deposited



Specimen C11 - Heat Treated

Figure 39. Molybdenum Tube Specimens Plated With 12.5  $\mu\text{m}$  (0.0005 In) of Chromium.

Specimens plated with 25 $\mu\text{m}$  of chromium appeared to be less porous and resist discoloration much better when compared to those with only 12.5  $\mu\text{m}$  of deposit.

The previous molybdenum cleaning and activation process was used on another molybdenum tube followed by an immersion in concentrated HCl for 20-30 seconds. The sample was transferred with voltage applied to a Platanex III bath at 2.15 A/dm<sup>2</sup> (20 ASF) for 20 minutes, and pulsed current was applied at a duty cycle of 80% and an average current density of 2.15 A/dm<sup>2</sup> (20 ASF). The coating failed before plating was completed. This process was repeated removing the HCl dip and substituting fluoboric acid, HF, 10% sulfuric acid, and cathodic activation in HCl. All parts had coating failures in the plating process.

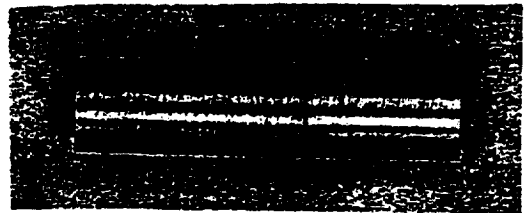
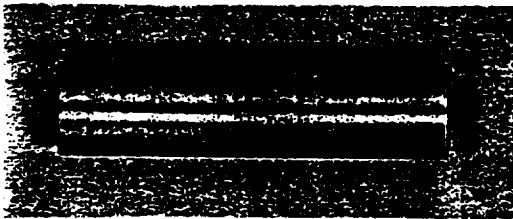
A further process was evaluated in which two samples were treated as follows:

1. Cleaned anodically in Oakite 90 with ultrasonics for 30 seconds followed by a soak with ultrasonics for 3-5 minutes and a rinse in deionized water.
2. Immersed in a solution of 100 g/l of KOH and 100 g/l of  $\text{K}_3\text{Fe}(\text{CN})_6$  at 60°C for one minute while stirring. Rinsed.
3. Electropolished in 50% by volume sulfuric acid and 50% by

by rinsing in running deionized water.

4. Immersed in a solution of 100 g/l of KOH and 100 g/l of K Fe(CN) at 60°C for 1 minute while stirring, and rinsed in running deionized water.
5. Electropolished in 50% by volume sulfuric acid and 50% by volume phosphoric acid anodically at 13 A/dm<sup>2</sup> (120 ASF) for 10 minutes, and rinsed in running deionized water for 1 to 2 minutes.
6. Repeated Step 4, and cathodically activated in concentrated HCl (37%) at 27.2 A/dm<sup>2</sup> (250 ASF) for 10 seconds.
7. Transferred with voltage applied to phosphate complexed platinum bath and struck at 27.2 A/dm<sup>2</sup> (250 ASF) for 10 seconds; decreased current density to 5.4 A/dm<sup>2</sup> for 30 minutes. Removed, rinsed, dried, and baked at 343°C for 1 hour.

Each sample was observed to show no signs of blistering or peeling after the bake or a tape peel test, Figure 40.



Specimen HCl-01 - As Deposited

Specimen HCl-02 - Heat Treated

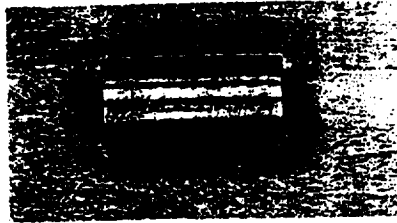
Figure 40. Molybdenum Plated With Platinum Over Chromium Strike.

In another process the specimens were activated and plated by the following procedure:

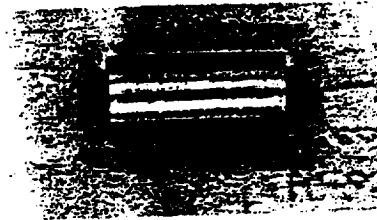
1. Processed according to Steps 1 through 5 of the prior process description.
2. Repeated Step 4 of the prior process.
3. Cathodically activated samples in concentrated fluoboric acid at 27.2 A/dm<sup>2</sup> (250 ASF) for 10 seconds and rinsed in concentrated HCl (37%) for 5 seconds.
4. Transferred with voltage applied to the phosphate complexed platinum bath to strike at 27.2 A/dm<sup>2</sup> (250 ASF) for 10 seconds followed by a reduction of current density to 5.4 A/dm<sup>2</sup> (50 ASF) for 30 minutes.

5. Rinsed, dried, and baked for 1 hour at 343°C (650°F).

Both samples showed no signs of peeling or blisters as shown in Figure 41. Heat treatment was at 1093°C for 1 hour.



Specimen F-04 - As Deposited



Specimen F-05 - Heat Treated

Figure 41. Molybdenum Specimens Coated With Chromium Using Cathodic Activation in Fluoboric Acid.

Specimen C08 was cut into two sections and renumbered "C12" and "C13". Chromium had been bonded successfully on this specimen which was part of the C06 and C07 group. These samples were processed as follows:

1. Cleaned anodically in 50 g/l Alconox detergent solution with ultrasonics for 30 seconds and soaked with ultrasonics for 4 minutes. Rinsing was in deionized water.
2. Etching with alternating current was performed in 0.15 g/l chromic acid at 71°C (160°F) and 5.4 A/dm<sup>2</sup> (50 ASF) for 5 minutes followed by rinsing and scrubbing until all brown residue was gone.
3. Cathodic activation in concentrated HCl was used at 27.2 A/dm<sup>2</sup> (250 ASF) for 10 seconds followed by rinsing in HCl.
4. Parts were transferred with voltage applied to phosphate complexed platinum electrolyte for striking at 27.2 A/dm<sup>2</sup> (250 ASF) for 30 seconds followed by current density reduction to 5.4 A/dm<sup>2</sup> (50 ASF) for 30 minutes.
5. Parts were rinsed, baked at 343°C, and one specimen was heat treated at elevated temperature in vacuum.

Specimen C13 was heat treated at 1538°C (2800°F) for 1 hour by TRW. Severe delamination was observed as shown in Figure 42. It can be concluded that specimens with a chromium interface have a temperature limitation that is less than needed for many applications in this program. With the Phase III needs for coatings that would resist oxidation at temperatures to 1760°C, or above, the further study of chromium coatings was abandoned in favor of other systems.

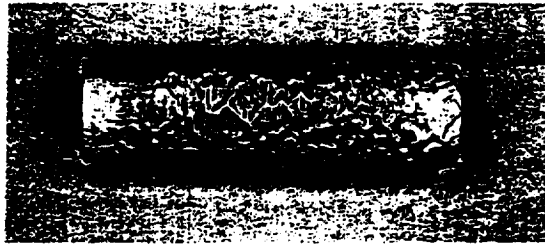


Figure 42. Coating Separation on Molybdenum Tube Containing An Interface Coating of Chromium and An Outer Coating of Platinum After Thermal Treatment at 1538°C.

### Rhenium as an Interfacial Coating

No work of significance with respect to rhenium plating as an intermediate coating for high temperature oxidation protection has been reported in the literature. Since rhenium has a very high melting point, it should be excellent as an intermediate coating for oxidizing environments in excess of 1500°C if properly protected by a barrier coating such as rhodium or platinum. The advantage of rhenium (or tungsten) as an interfacial coating on certain refractory metals and alloys is the ability to stop, or at least retard, diffusion of the coating into the substrate, or the reverse. This can be a major factor of importance if the coating forms Kirkendall voids at the interface at elevated temperatures.

Two rhenium plating baths were used in this study having compositions and operating conditions as follows:

#### 1. Rhenium Sulfate Bath

Rhenium Metal	5 g/l
Sulfuric Acid	5 ml/l
Temperature	65.6°C
Anodes	Platinized Ti
Pulse Current Conditions	
Ave. Current Density	25 A/dm <sup>2</sup> (230 ASF)
Peak Current Density	250 A/dm <sup>2</sup> (2300 ASF)
Duty Cycle	10%
Time On	1 msec
Time Off	10 msec

#### 2. Phenium Phosphate Bath

Rhenium Metal	10 g/l
Ammonium Hydroxide	80 ml/l
Phosphoric Acid (to pH 5.7)	142 ml/l minimum
Temperature	65.6°C
Anodes	Platinized Ti
Pulse Current Conditions	
Ave. Current Density	25 A/dm <sup>2</sup> (230 ASF)
Peak Current Density	250 A/dm <sup>2</sup> (2300 ASF)

Duty Cycle  
Time On  
Time Off

10%  
1 msec  
10 msec

Initial efforts to deposit rhenium on molybdenum involved the same preparation procedure used to plate platinum on molybdenum, except that rhenium sulfate electrolyte was used for the rhenium deposit. Use of rhenium phosphate baths for the initial rhenium deposit was not successful. As a result, the procedure adopted was:

1. Detergent clean and rinse the molybdenum specimen.
2. Electropolish for 3 to 5 minutes in a 1:1 ratio solution of sulfuric and phosphoric acids making the part anodic at  $9.8 \text{ A/dm}^2$  (90 ASF). Rinse.
3. Etch in a solution of 100 g/l  $\text{K Fe(CN)}_6$  and 100 g/l KOH for 1 minute at  $60^\circ\text{C}$  ( $140^\circ\text{F}$ ). Rinse.
4. Cathodic activate in concentrated HCl for 30 seconds at  $32.6 \text{ A/dm}^2$  (300 ASF) followed by cathodic activation in 50% by volume sulfuric acid at  $32.6 \text{ A/dm}^2$  (300 ASF).
5. Transfer immediately, with voltage applied, to the rhenium sulfate bath and strike at  $24 \text{ A/dm}^2$  (220 ASF) for 5 minutes; set pulse at 1 msec on and 10 msec off, plating for 90 minutes.

This sample was heat treated in air at  $371^\circ\text{C}$  ( $700^\circ\text{F}$ ) for 1 hour. After cooling, a tape test was performed. Some dark powder was removed by the tape, but a continuous adherent layer of rhenium remained.

Other samples were processed in similar manner and activations applied for plating neutral phosphate complexed platinum over the rhenium. None of the procedures was satisfactory. A change was made to initiate plating with the Platanex III bath because of the low pH of this bath and the ability to cover the surface quickly with platinum. Various rhenium activation immersion treatments were tried, including hot concentrated sulfuric acid and sulfuric acid with cathodic activation current. Platinum could be deposited over the rhenium but there was not an adequate bond.

Additional samples of molybdenum were plated with rhenium from the sulfate bath followed by rhenium from the phosphate bath. A heat treatment at  $1538^\circ\text{C}$  in vacuum failed to consolidate the rhenium coating which degraded into a black powder. This work indicated that the rhenium must be made more tarnish resistant as might best be achieved by use of higher average and peak current

densities based on Task I studies.

TRW furnished some C103 alloy rods for substrates for the investigation of rhenium interface coatings to prevent Kirkendall void formation. A procedure that had been used to activate Ta-10W for rhodium plating was adapted to this alloy. The process was:

1. Degrease in acetone for 2 - 3 minutes and air dry.
2. Ultrasonic alkaline clean in Oakite 90 (45 to 60 g/l) for 10 minutes at 49° to 71°C. Ultrasonic rinse at 45°C for 3 minutes.
3. Rinse in running deionized water for 3 minutes; drain part well.
4. Acid pickle in a solution of 28 vol % nitric acid (70%), 16 vol % HF (48%), 28 vol % sulfuric acid, and 28 vol % water. Stir the solution continuously and pickle part for 20 to 60 minutes (or until at least 0.0003 in of metal is removed). Rinse in running deionized water for at least 3 minutes.
5. Cathodically activate in 66 vol % sulfuric acid at 27.2 to 32.6 A/dm<sup>2</sup> (250 to 300 ASF) for 60 seconds; immerse quickly in 15 vol % sulfuric acid.
6. Transfer, with fairly high voltage applied, into a rhenium sulfate bath with 108.7 A/dm<sup>2</sup> (1000 ASF) current density for 30 seconds.
7. Transfer to the rhenium sulfate bath with no rinse and a current density of 108.7 A/dm<sup>2</sup> for 30 more seconds; set the pulse for 1 msec on and 10 msec off and adjust power supply for an average current density of at least 230 A/dm<sup>2</sup> (2300 ASF).

Specimens thus treated were submitted for a scanning electron microscope study at TRW, Redondo Beach, CA. Figure 43 shows a view of the rhenium deposit surface at a magnification of 100 power. The structure appears grainy and somewhat porous. Figure 44, at a magnification of 400 power, confirms the porosity. This underscores the need for further development of rhenium plating in order to produce pore-free deposits that will remain stable for longer periods of time in hostile environments. This coating eventually degraded on exposure to the laboratory environment. A possible means for improving the performance of such rhenium coatings might be a heat treatment in hydrogen at a temperature above 1000°C.

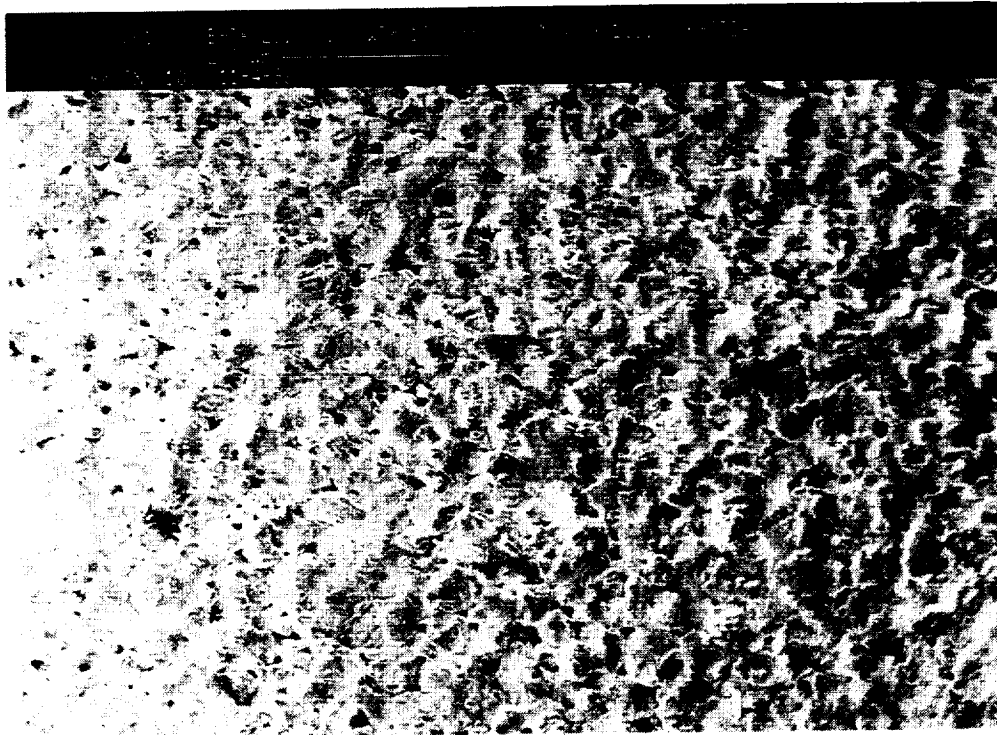


Figure 43. Scanning Electron Microscope View of Electrodeposited Rhenium Surface Topography Over C-103 Alloy Substrate. Magnification 100X. (Courtesy TRW, Inc., Redondo Beach, CA)

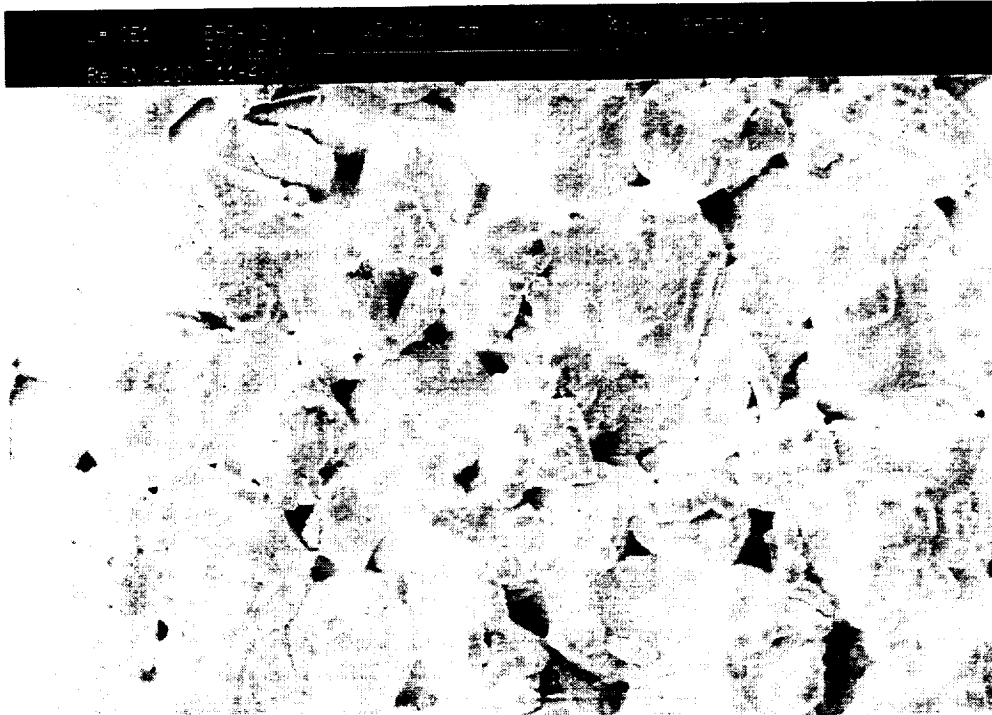


Figure 44. Scanning Electron Microscope View of Electrodeposited Rhenium Surface Topography Over C-103 Alloy Substrate. Magnification 400X. (Courtesy TRW, Inc., Redondo Beach, CA)



TASK II - INVESTIGATION OF HIGH INTEGRITY BONDING AND DIRECT  
DEPOSITION PROCEDURES FOR PLATINUM GROUP METALS  
AND INTERFACIAL COATINGS  
PART B - DIRECT DEPOSITION ONTO REFRACTORY AND INTERMEDIARY  
COATINGS

**Background**

This portion of the program is concerned with preparation of various substrates to obtain high integrity bonding of directly applied deposits of the platinum metals group. Also of concern is the ability to build thick deposits (50  $\mu\text{m}$ , or more) of these metals in multiple layers without laminations or blistering. It has generally been considered in the literature that a thick deposit is one of 2 to 12.5  $\mu\text{m}$ ; however, such deposits are usually porous until a thickness of 50 to 100  $\mu\text{m}$  (0.002 to 0.004 in) is obtained.

Avoidance of porosity is a very difficult problem in that it is not only affected by the plating bath and operating conditions, but is equally influenced by the substrate surface preparation with respect to cleanliness. Hydrated salts from chemical pickling and etching operations are not always visible, and special treatments may be needed for their removal. Each metal or alloy usually requires a unique preparation sequence for producing high integrity bonds with metal coatings. In this portion of the program, preparation for bonding of specific substrates are examined based on preferred use as engineering structural materials in on-going aerospace and commercial needs.

**Plating on Molybdenum and Alloys**

The literature suggests many processes for depositing adherent coatings on molybdenum. Levy, Arnold, and Ma [39] used the following process to deposit gold on unalloyed molybdenum:

1. Alkaline ferricyanide etch for 10 seconds at room temperature in a solution of 200-250 g/l potassium ferricyanide and 75-85 g/l potassium hydroxide. Water rinse.
2. Dip in 50 vol % HCl for 10 seconds at room temperature. Water rinse.
3. Acid gold strike 1 to 3 minutes at 0.1 to 0.2 A/dm<sup>2</sup> (1 to 2 ASF) to deposit 0.06 to 0.37  $\mu\text{m}$  of gold. Water rinse and dry.
4. Diffuse in dry hydrogen at 830°C (1525°F) for 30 minutes.
5. Acid gold strike 4 minutes at 0.1 to 0.2 A/dm<sup>2</sup> to deposit an additional 0.2 to 0.5  $\mu\text{m}$  of gold.

6. Repeat the dry hydrogen diffusion step after a rinse.
7. Acid gold strike for 45 to 75 seconds at 0.1 to 0.2 A/dm<sup>2</sup> (1 to 2 ASF). Water rinse.
8. Plate with desired metal.

They noted that the first gold applied had limited bond strength and that thicker gold was prone to peel. Hydrogen heat treating was necessary to cause slight diffusion for good adherence. The solubility of gold in molybdenum is exceedingly small, hence the gold layer remains as an interface to the subsequent metal plate. Any existing gold layer would be detrimental in the present work, since the service temperatures are above the gold melting point.

These same investigators deposited rhodium onto TZM alloy by the following process:

1. Solvent degease and alkaline clean at 80°C for 5 minutes. Water rinse.
2. Alkaline ferricyanide etch with agitation for 30 seconds at room temperature. Water rinse.
3. Sulfuric acid (5-10 vol %) dip for 10 seconds. No rinse.
4. Rhodium strike in an acid rhodium bath at 1.1 to 2.1 A/dm<sup>2</sup> (10-20 ASF) and 50°C to deposit 0.05-0.08 μm (2-3 μin) of rhodium. Water rinse and dry.
5. Diffusion heat treat at 1000°C (1830°F) for 30 minutes in vacuum; purge with helium.
6. Sulfuric acid dip for 30 seconds minimum at room temperature.
7. Rhodium plate as in Step 4 to a thickness of 0.5 μm (20 μin). Water rinse and dry.

They noted similar behavior of the acid rhodium sulfate bath to that found in the present studies. Magnesium sulfamate as a stress reducer tended to break down with use to convert sulfamate to sulfate. This combined with rhodium sulfate replenishment additions caused the bath specific gravity to rise. This resulted in stress problems requiring more stress reducer to keep the plate adherent. This is why conversion to selenic acid and means for removal of excess sulfates were developed in this program.

Mikkola and Daugherty [40] developed processes to plate electroless nickel directly on molybdenum with a chromic/nitric acid etch in place of the alkaline ferricyanide solution as follows:

1. Preclean by pumice scrubbing or conventional alkaline cleaning. Water rinse.
2. Anodic etch in a solution of  $\text{CrO}_3$  (10% by weight) and 71% nitric acid (10% by vol) at room temperature and  $15.5 \text{ A/dm}^2$  (144 ASF) for 1 minute. Water rinse.
3. Anodic treatment in 50% aminotrimethylene phosphonic acid (ATMP) (25% by vol) at room temperature and  $15.5 \text{ A/dm}^2$  (144 ASF) for 4 minutes. Water rinse.
4. Oxide film removal in  $\text{CrO}_3$  (10% by weight) and 71% nitric acid (10% by vol) at room temperature for 1 minute. Water rinse.
5. Nickel strike in electroless nickel bath at 5 volts for 15 seconds, and plate electroless nickel (no current) to a minimum thickness of 0.25 mm.

The above process has an advantage in the fact that heat treatments are not required.

Troup [41] developed direct deposition of chromium onto molybdenum substrates using conventional cleaning and pickling of the metal followed by cathodic acid activation. This was accomplished by making the molybdenum cathodic in a strong acid and passing current through the solution at a density of at least  $25 \text{ A/dm}^2$  (230 ASF) for 5 to 15 seconds. Carbon anodes were used to withstand the strong acid while remaining inert. The process is described as liberating hydrogen at the cathode which (1) reduces molybdenum oxide to metallic molybdenum and (2) forms a hydride with molybdenum which has a limited stability time. This delays oxide formation to permit direct plating on the molybdenum.

This latter method, termed cathodic acid activation (CAA), was shown to produce best adhesion to many of the refractory metals and alloys used in this program. The process steps were:

1. Ultrasonic clean in Alconox (15-22.5 g/l) at  $40^\circ\text{C}$  for at least 10 minutes. Reclean as necessary. Water rinse.
2. Etch in 50 vol % sulfuric acid and 50 vol % nitric acid for 30 to 60 seconds. Rinse.
3. Pickle in a solution of 100 g/l potassium ferricyanide and 100 g/l potassium hydroxide for 30 seconds, or until the surface appears uniformly etched. Rinse.
4. Cathodically treat in concentrated  $\text{HCl}$  (37%) at  $27.2 \text{ A/dm}^2$  for 10 to 15 seconds, and transfer with voltage applied to a chloride based plating bath such as the hexachloroplatinate bath complexed with phosphates.

A second cathodic activation in an acid compatible with the plating bath could be performed to permit immediate plating without drag-in of undesired salts. For example, a cathodic acid treatment in sulfamic acid could be used before plating in a Platanex III bath, or cathodic activation in a 30-50 vol % sulfuric acid bath could be used before plating in a rhodium sulfate bath or a rhenium sulfate strike bath.

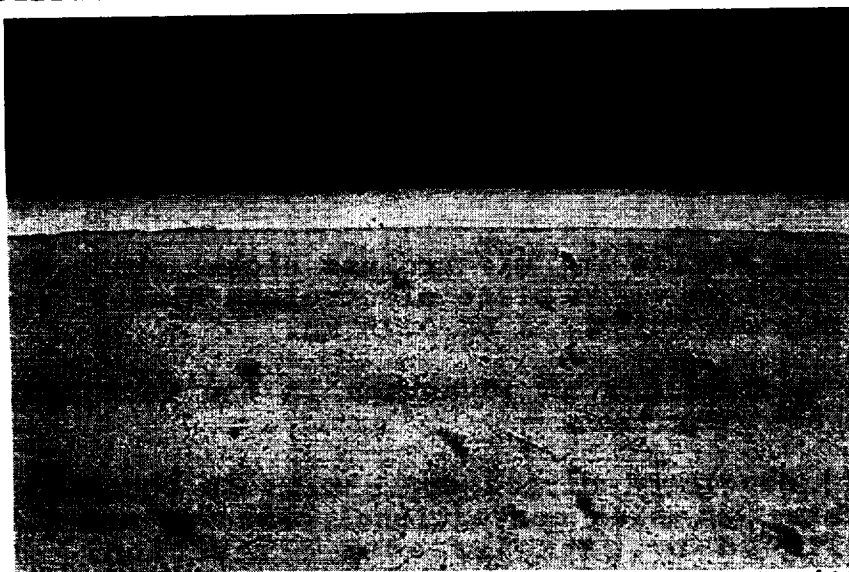


Figure 45. Photomicrograph of Molybdenum Rod With 50  $\mu$ m of Platinum Plated from Phosphate complexed Bath. Magnification 200X.

Mo-47Re alloy proved to be a more difficult substrate on which to obtain adherent coatings. In developing chemical treatment processes, it was necessary to examine the effects of various reagents on both elements of the alloy as well as any of the platinum group metals that might be deposited. Table XX shows effects of various acids and alkalies on molybdenum and rhenium - as well as the platinum group metals.

TABLE XX - ATTACK BY REAGENTS ON SELECTED REFRACTORY AND PLATINUM GROUP METALS

REACTING CHEMICAL	MOLYBDENUM	RHENIUM	IRIDIUM	RHODIUM	PLATINUM
Agua Regia (20 C)	Rapid Att.	Rapid Att.	No Attack	No Attack	Rapid Att.
HCl, 36% (20 C)	No Attack	No Attack	No Attack	No Attack	No Attack
HF, 40% (20 C)	No Attack	No Attack	No Attack	No Attack	No Attack
Nitric, 70% (20 C)	Slt. Att.	Rapid Att.	No Attack	No Attack	No Attack
Sulfuric, 98% (100 C)	Sig. Att.	Sig. Att.	No Attack	Slt. Att.	No Attack
Sulfuric, 98% (20 C)	Slt. Att.	Slt. Att.	No Attack	No Attack	No Attack
Nitric + HF (20 C)	Slt. Att.	Rapid Att.	No Attack	Slt. Att.	No Attack
Sulf. + HCl (20 C)	Slow Att.	Slow Att.	No Attack	Slow Att.	No Attack
Aqueous Alkalies	No Attack	Slow Att.	No Attack	No Attack	No Attack

Two other Mo-47Re specimens were plated with iridium from fused salt electrolyte to thicknesses less than 50  $\mu\text{m}$  (0.002 in). They were identified as MORE-IR-PT-08 and 09. Specimen 09 was plated with iridium using uncoated stainless steel fixturing. Specimen 08 fixturing was plated with nickel followed by platinum. Each sample was plated to just under 38  $\mu\text{m}$  (0.0015 in) of platinum from an aqueous neutral phosphate complexed platinum bath. Both samples failed in oxidation testing at times under 30 hours as shown in Figure 49. This failure is believed due to the fact that the iridium coat had more porosity due to a thickness less than that applied to Specimen MORE-IR-02. Introducing this sample to activating solutions for aqueous platinum plating may have attacked the base metal to produce hydrated salts in pores

Specimen MORE-IR-02 was plated with iridium from the fused salt bath to a thickness of about 63  $\mu\text{m}$  (0.0025 in) and tested in a static oxidation environment at 1260°C for 30 hrs. The coating exhibited very good oxidation performance as shown in Figure 46. Sections cut from the oxidation tested sample were examined on a scanning electron microscope by Pratt & Whitney GESP Division, West Palm Beach, FL where the oxidation testing was also performed. Figure 47 shows the coating profile after oxidation testing. There is a roughness to the surface which is typical for iridium coatings of thickness deposited in few coating runs. A view at a higher magnification, Figure 48, shows what appears to be a thin diffusion layer between the iridium and the substrate.

4. Preheat in a separate crucible furnace with an argon purge and transfer to the fused salt iridium bath for plating.
3. Soak in 50 vol % fluoboric acid (48%) and rinse. This was later changed to HCl which does not attack Mo-47Re. Rinse in deionized water and dry with clean, filtered argon gas.
2. Ultrasonic cleaning in Oakite 90 alkaline solution at 50°C for 10 minutes followed by ultrasonic rinsing at the same temperature.
1. Light mechanical scrubbing with gray Scotchbrite pads for removal of bulk surface oxides and contaminants.

plating consisted of:  
preparing rhenium and molybdenum-rhenium alloys for fused salt dry the sample before molten salt entry. The process used for a clean surface could not be used because of the time required to normal cathodic activation treatment to deter oxide formation on For depositing iridium on this alloy from fused salt baths, the attack and must be removed by heat treating at 1538°C (2800°F). A sigma phase is often present which is susceptible to pitting Little is known about the corrosion behavior of Mo-47Re; however,

# Coatings on Mo-47.5Re Oxidation Evaluation

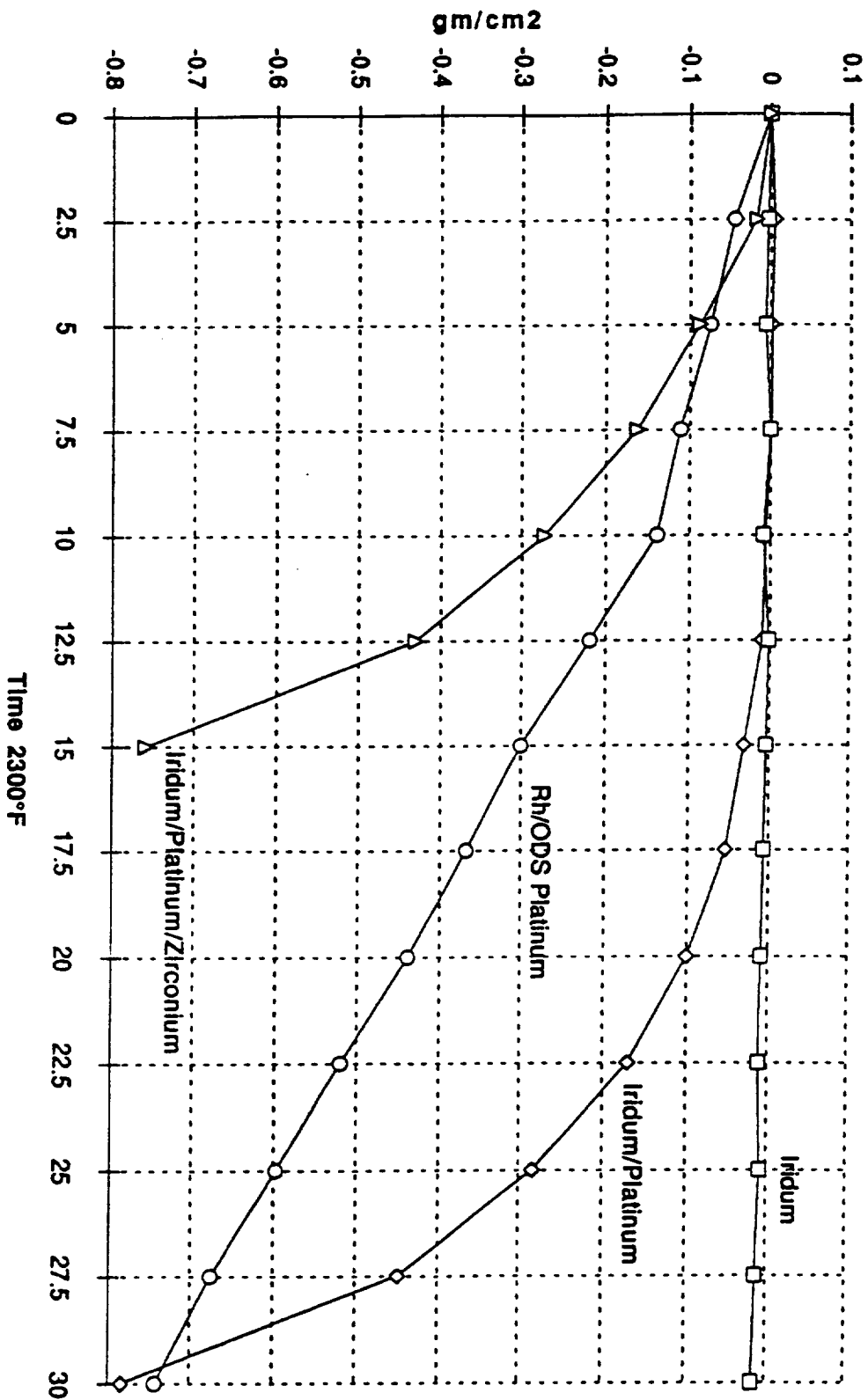


Figure 46. Oxidation Performance of Platinum Group Metal Electrodeposits on Mo-47Re Alloy

2-2

- 87 -

Figure 48. Scanning Electron Microscope Examination of 63  $\mu$ m Thick Iridium Coating on Mo-47Re Specimen MORE-Ir-02 After Static Oxidation Testing at 1260°C (2300°F). Magnification 500X. (Courtesy Pratt & Whitney)

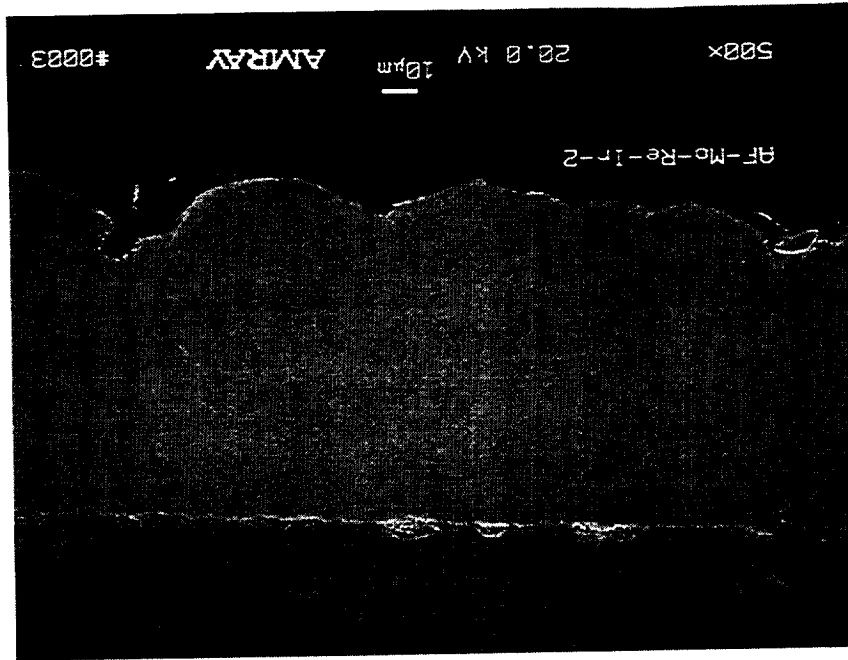
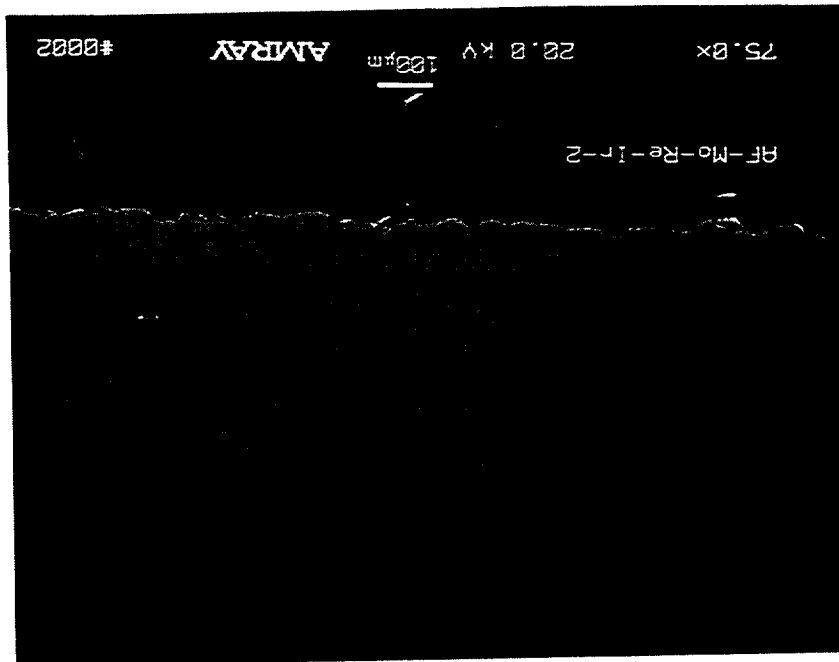


Figure 47. Coating Profile of 63  $\mu$ m Thick Iridium Coating on Mo-47Re Alloy After Static Oxidation Testing at 1260°C (2300°F) For 30 Hours. Magnification 75X. (Courtesy Pratt & Whitney)



# Pt/Ir on Mo-47.5Re Oxidation Data

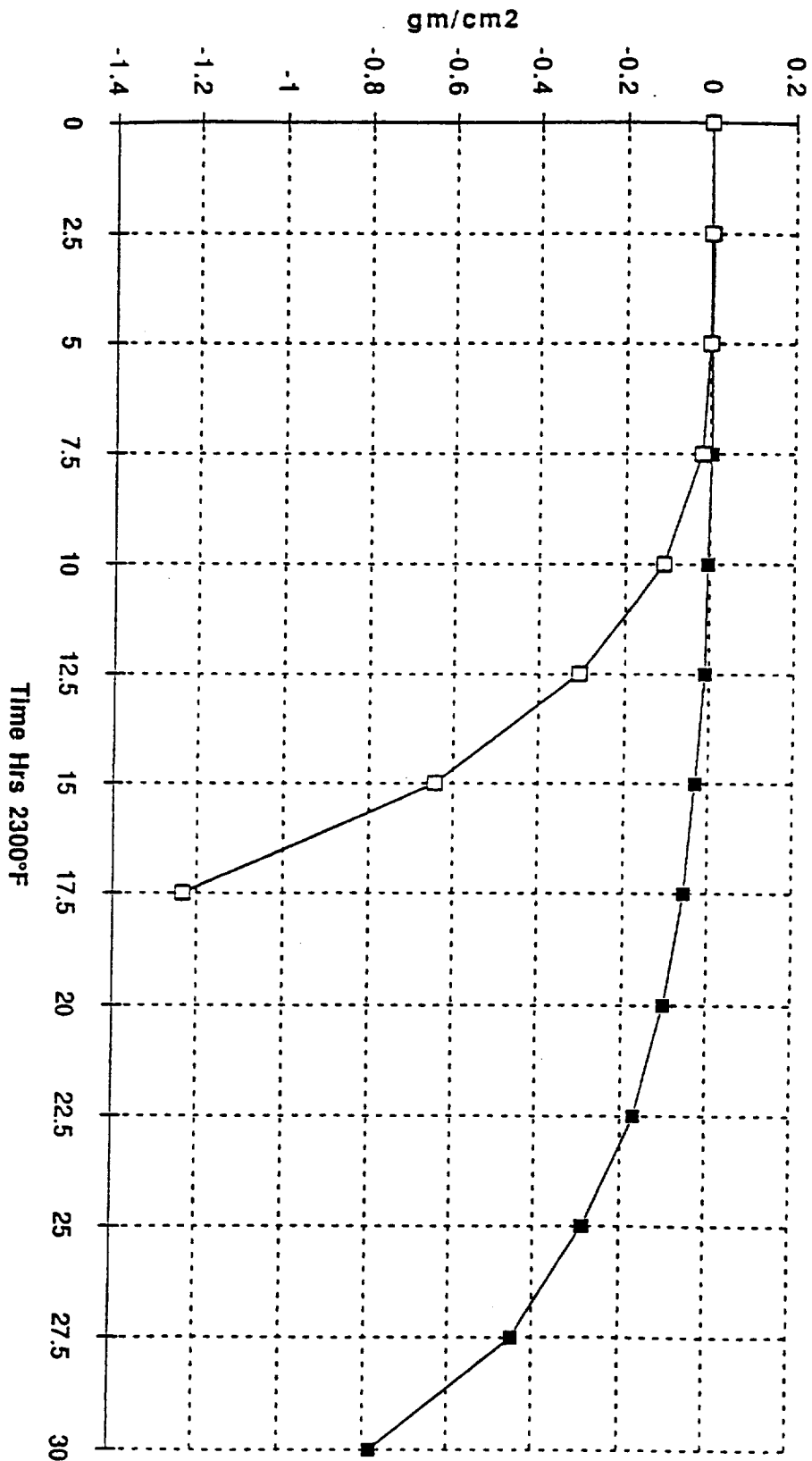
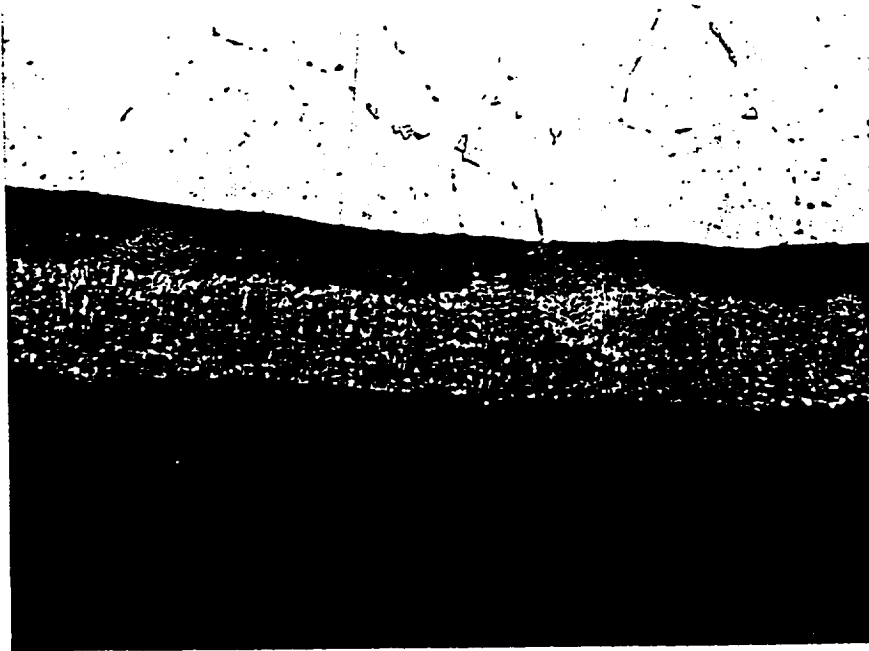


Figure 49. Oxidation Performance of Aqueous Bath Platinum Over Iridium Molten Salt Bath Deposits on Mo-47Re Alloy



Figure 51. Scanning Electron Microscope Evaluation of Platinum Plated Mo-47Re Sample After Static Oxidation Testing at 1260°C.



Mo-47.5 RE

Interaction Zone

This specimen was not isostatic pressurized by Pratt & Whitney for 4 hours at 1204°C (2200°F) and 20 ksi pressure. Oxidation testing was conducted for 30 hours at 1260°C (2300°F) with very good performance over the first 20 hours and gradual degradation believed due to sample edge defects, Figure 51. Other methods of coating are compared in this figure. A section of this sample

polishing with Scotchbrite). The prior platinum surface and remove any Nylon residue from rinsed, and soaked in hot concentrated sulfuric acid (to activate was polished with green Scotchbrite, ultrasonic alkaline cleaned, 100  $\mu$ m (0.004 in) of platinum. Between each run, the specimen Seventeen platinum plating runs were used to build a thickness of applied to the neutral phosphate complexed chloroplatinate bath. in concentrated hydrochloric acid, and transferring with voltage tion consisted of ultrasonic alkaline cleaning, rinsing, soaking had to be modified because of the thin rhodium layer. Preparation thicker than 1 or 2  $\mu$ m. The method of activating the specimen initially coated with a thin film of rhodium estimated to be no A Mo-47Re sample was provided by Pratt & Whitney which had been

that reacted under high temperature. Two other specimens plated with aqueous platinum over fused salt iridium were plasma coated with zirconium. Upon heating to high temperature a very brittle intermetallic compound was formed which ruptured the coating and resulted in premature failure as noted in Figure 46.

# Pt Coated Mo-Re Oxidation Evaluation (Static)

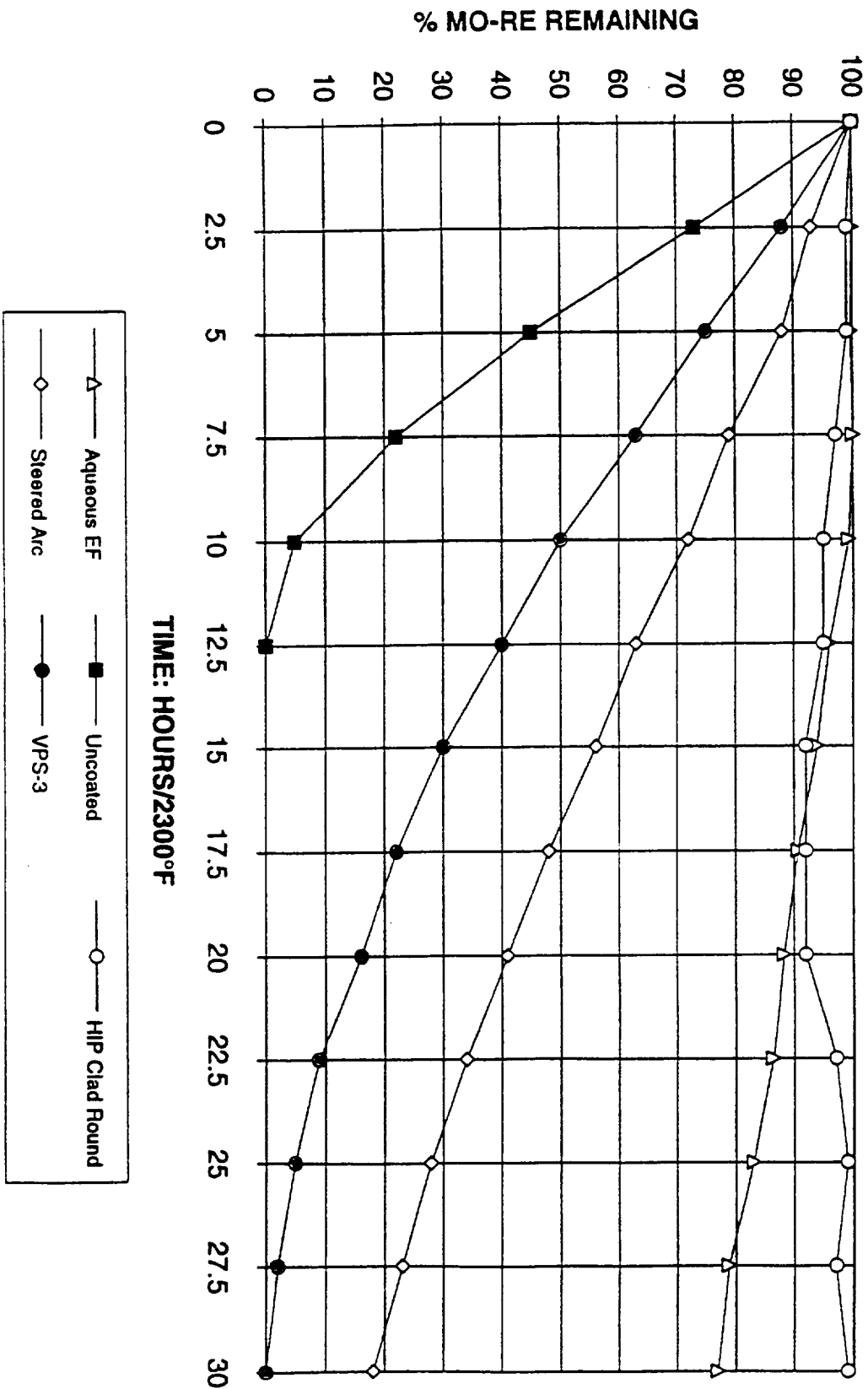


Figure 50. Results of Static Oxidation Tests on Mo-4/Re Coated With 17 Layers of Platinum From a Neutral Aqueous Electrolyte.

after oxidation testing was examined by scanning electron microscope and indicated what appeared to be a separation of the entire coating system from the Mo-47Re, Figure 51. The entire protective coating could be separated as a sheath from the Mo-47Re. This prompted a re-examination of the activating and bonding system for this alloy. The modified process became:

1. Sand the surfaces of the Mo-47Re alloy with 320 grit Wet-Dry sand paper to remove bulk surface oxides and other contaminants. Detergent clean with scrubbing. Rinse.
2. Ultrasonic alkaline clean for 10 minutes minimum at 49°C (120°F) and rinse in deionized water for 2 minutes.
3. Soak in a solution of 100 g/l K Fe(CN) and 100 g/l KOH at 80°C for 1 minute to 5 minutes (based on age of this etching solution. Rinse in hot water (80°C).
4. Soak in 50 vol% nitric acid (71%) at room temperature for 10 to 30 seconds - or until all rhenium smut is removed from the surface. Rinse in deionized water.
5. Soak in 30% hydrogen peroxide for 30 seconds and check for gassing at the Mo-47Re surface. If gassing is heavy, repeat Steps 3 through 5. Once gassing is minimal, if any, rinse the part in fresh deionized water, and immediately proceed to the cathodic acid activation.
6. Perform cathodic acid activation at  $27.2 \text{ A/dm}^2$  (250 ASF) for 15 to 30 seconds using room temperature acid. The choice of acid shall be:
  - a. Concentrated HCl (37%) for phosphate complexed platinum.
  - b. 33-50 vol % sulfuric acid (96%) for acid rhodium sulfate or rhenium sulfate.
  - c. Concentrated sulfamic acid for Platanex III.
7. Transfer with voltage applied from the cathodic acid activation bath into the plating bath for application of a strike plate to cover the Mo-47Re surface as rapidly as possible. Strike current density should be as high as possible without causing burning at the electrical contacts. Decrease current density after 1 to 2 minutes to normal range and plate for required thickness.

This process was found to apply to almost any deposition coating required on this alloy. It was also useful in rework or repair of localized coating defects. Rhodium plated on this alloy using this process could only be removed by mechanical means such as grinding or machining. The process also led to adherent deposits of acid gold and nickel over a Wood's nickel strike.

## Plating on Tungsten

Marzano [41] noted that tungsten is not attacked by the common mineral acids. The usual cleaning and pickling treatments failed to produce adherent plated coatings. His studies indicated that the following process was effective for bonding deposits:

1. Degrease and abrasive clean to remove heavy oxides and soak in a hot alkaline cleaner at 60° to 72°C (140°-160°F) for 1-2 minutes. Rinse in water.
2. Acid dip in a solution composed of:  
37.5% by volume concentrated HF (48%)  
12.5% by volume concentrated nitric acid (70-71%)  
50.0% by volume water  
Temperature ..... room  
Time..... 2-5 minutes  
Container..... Polyethylene
3. Rinse in water.
4. Anodic etch in a hot alkali solution of:  
KOH..... 30% by weight  
Temperature..... 50°-60°C (120°-140°F)  
Current density..... 10-30 A/dm<sup>2</sup> (100-300 ASF)  
Time..... 2-5 minutes  
Cathodes..... Steel
5. Quickly rinse in water.
6. Plate in a strike bath after first dipping part in 10% sulfuric acid solution for 1 minute and quickly rinsing. Enter strike bath with voltage applied.

Marzano mentions only strike baths of chromium, nickel, copper, and gold. However, it would appear possible to strike some of the platinum group metals on tungsten treated in this manner.

Groshart [38] suggests a similar process, except:

1. The anodic etch is performed in a solution containing NaOH at 3.7-15.0 g/l, at a temperature of 56.7°-62.8°C (135°-145°F), and the time being that required to remove scale.
2. Activation is in a 20 to 40 vol % HF solution at room temperature using 4 to 6 volts ac. This is followed by immediate plating in an acid plating bath.
3. An alternate activation can be performed by anodic etching in the same manner described by Marzano.

The following process proved satisfactory in the present study:

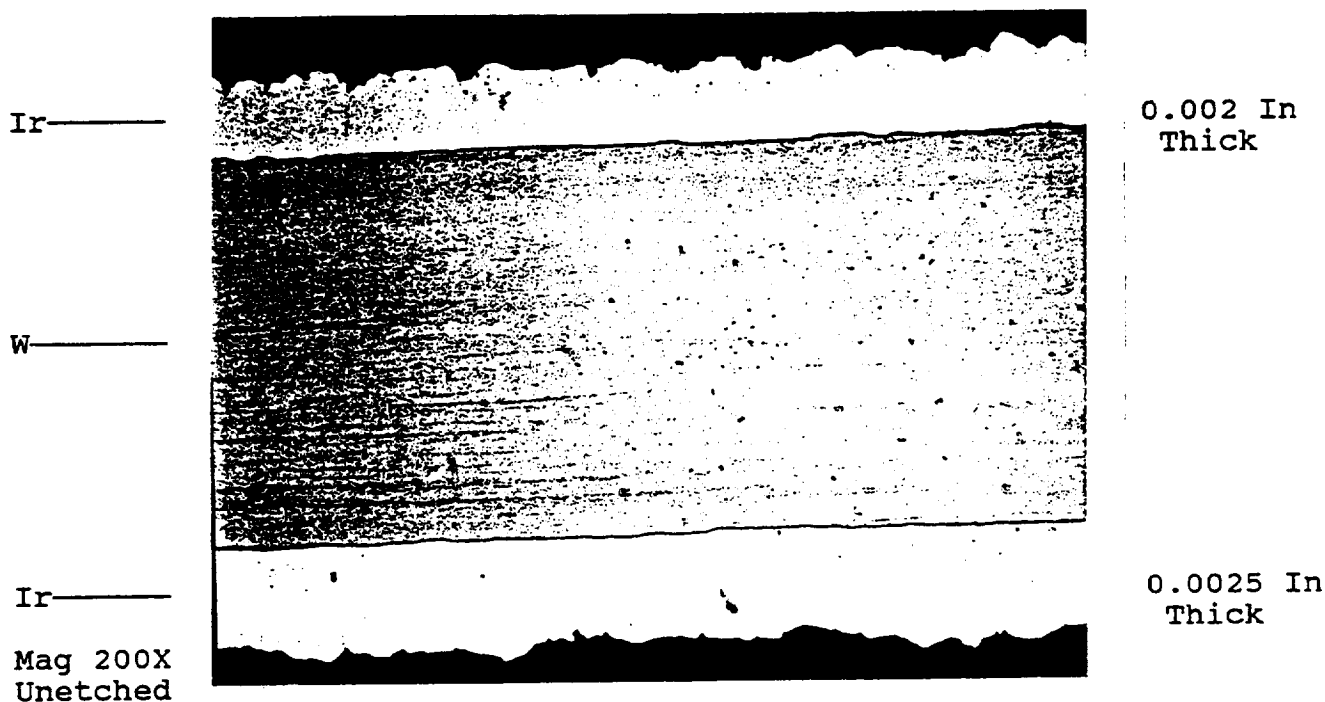
1. Degrease in acetone for 5 minutes, air dry, ultrasonic clean in Oakite 90 for 5 minutes at 48.9°C (120°F), and rinse ultrasonically in deionized water followed by a second rinse in running deionized water.
2. Treat the tungsten surface anodically in 20% by weight NaOH at 71.1°C (160°F) and 21.7 A/dm<sup>2</sup> (200 ASF) for three minutes minimum (longer times are necessary as this solution ages). The cathode is stainless steel. The removal of 25 to 50 μm (0.001-0.002 in) of tungsten is desired. Rinse in running deionized water for 3 minutes.
3. Treat the part in 30% by weight HF (48%) at room temperature using 5.4 A/dm<sup>2</sup> (50 ASF) alternating current at 60 Hertz for 2 minutes. The second electrode is platinized titanium. Rinse in deionized water.
4. Activate cathodically in 66% by volume sulfuric acid at 27.2 A/dm<sup>2</sup> (250 ASF) using graphite anodes. Quickly rinse in 15 vol % sulfuric acid to remove any carbon particles.
5. Transfer with voltage applied to the strike or plating bath.

If plating from a fused salt bath is required, the part may be immersed in a molten eutectic cyanide bath to clean, dry, and adjust substrate temperature before entering the fused salt plating bath. This may be done after Step 3 above. Figure 52 shows good adherence of iridium plated on tungsten from a fused salt bath. The specimen was metallurgically evaluated before and after heat treating at 1427°C (2600°F) in vacuum for six hours. This demonstrates the capability of tungsten as a diffusion barrier, since there is no sign of Kirkendall voids or diffusion at the interface of the iridium and tungsten.

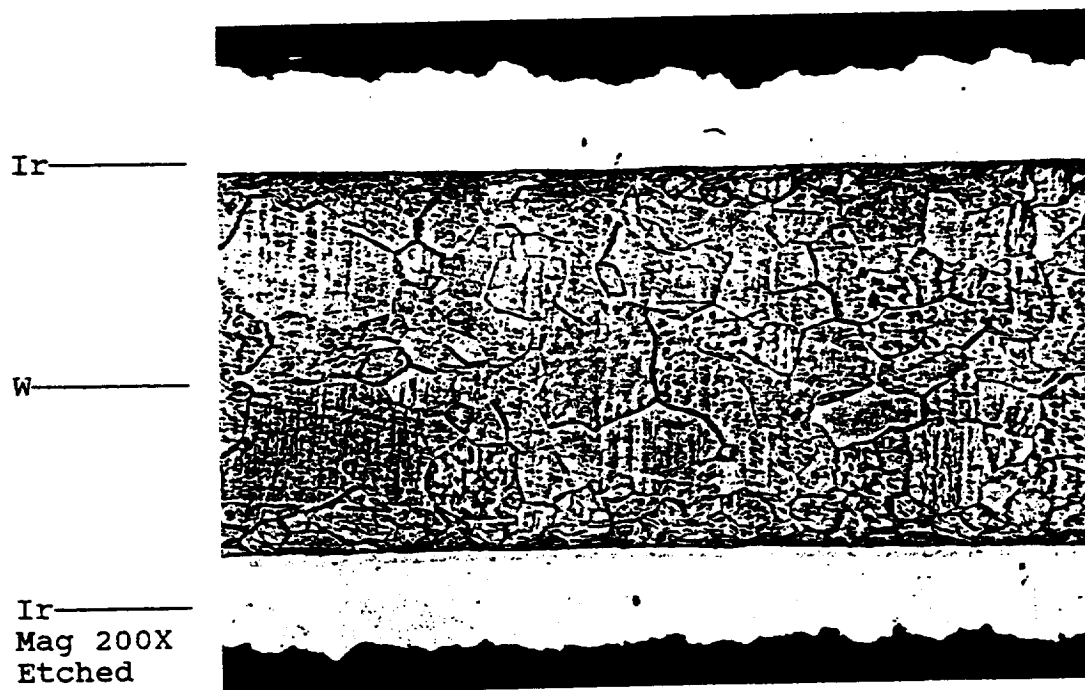
#### Plating on Tantalum Alloys

No specific preplating processes were found in the literature, so it was necessary to develop such a process in this program. The process that appeared to work best was:

1. Degrease in acetone for 1 to 3 minutes, air dry, ultrasonic clean in Oakite 90 (or other suitable commercial cleaner) at 45 to 60 g/l at 49° to 71°C (120°-160°F) for 8 to 12 minutes. Rinse in deionized water for 3 to 4 minutes.
2. Acid pickle in a room temperature solution of 28% by volume nitric acid, 16% by volume HF, 28% by volume sulfuric



Molten Salt Iridium Deposits on Tungsten Substrate - As Deposited



Iridium-Tungsten Interfaces After Thermal Exposure of 2600 F  
in Vacuum for Six Hours

Figure 52. Evaluation of Tungsten as a Diffusion Barrier for  
Iridium Electrodeposits on Substrates Susceptible to  
Kirkendall Voids. (Courtesy TRW, Redondo Beach, CA).

acid, and 28% by volume water. Pickling time is 20 to 60 minutes (pickling rate should be established on separate specimens). Rinse in deionized water for 3 to 5 minutes.

3. Activate the part with a cathodic treatment in 66% by volume sulfuric acid in deionized water at room temperature for 1 minute at  $27.2 \text{ A/dm}^2$  (250 ASF) using graphite as an anode.
4. Transfer immediately to a strike or plating bath with voltage applied. If the strike bath or plating bath is not compatible with sulfate ion, substitute the appropriate acid (i.e.- HCl, sulfamic, etc.) in Step 3. If the deposit to be applied is from a fused salt bath, dry the part after Step 3 using clean filtered argon, and immerse the part in a molten eutectic cyanide bath for cleaning and preheating before entering the plating cell.

This pretreatment process was used to deposit iridium from a fused salt bath onto Ta-10W, a tantalum based alloy often used in the aerospace industry as a high temperature structural material. The specimen was heat treated in vacuum at  $1482^\circ\text{C}$  ( $2700^\circ\text{F}$ ) for 1 hour and sectioned for metallurgical evaluation. Figure 53 shows the formation of Kirkendall voids at the interface due to rapid diffusion of one element into the other. This effect limits the application of plated platinum group metal coatings on some substrates. However, development of improved rhenium interface deposits is expected to provide sufficient diffusion resistance as to make such coatings practical.

#### Plating on Platinum Group Metals

Because of their highly noble characteristics, many metals of the platinum group are difficult to plate upon with a bond of high integrity. Cathodic activation in a concentrated acid compatible with the platinum group metal plating bath were used but found to be unreliable due to excessive hydrogen build-up in the previous deposit. Dipping the part in various acids also did not provide reliable bonds. Because thin platinum group metal deposits were still porous, salts could accumulate in these pores leading to difficulty in removal. Scrubbing the surfaces of the previous coatings - particularly platinum - to remove smut, usually left a residual from the item used in the scrubbing operation (i.e., Nylon from Scotchbrite).

It was found that 30% hydrogen peroxide was effective in removing these contaminants from rhodium, platinum, or iridium plated surfaces, but there was also attack on the platinum group metal. It was found that hot concentrated sulfuric acid immersion followed by a hot water soak to remove salts from pores and dissolve Nylon was the most effective procedure for plating restarts. However,

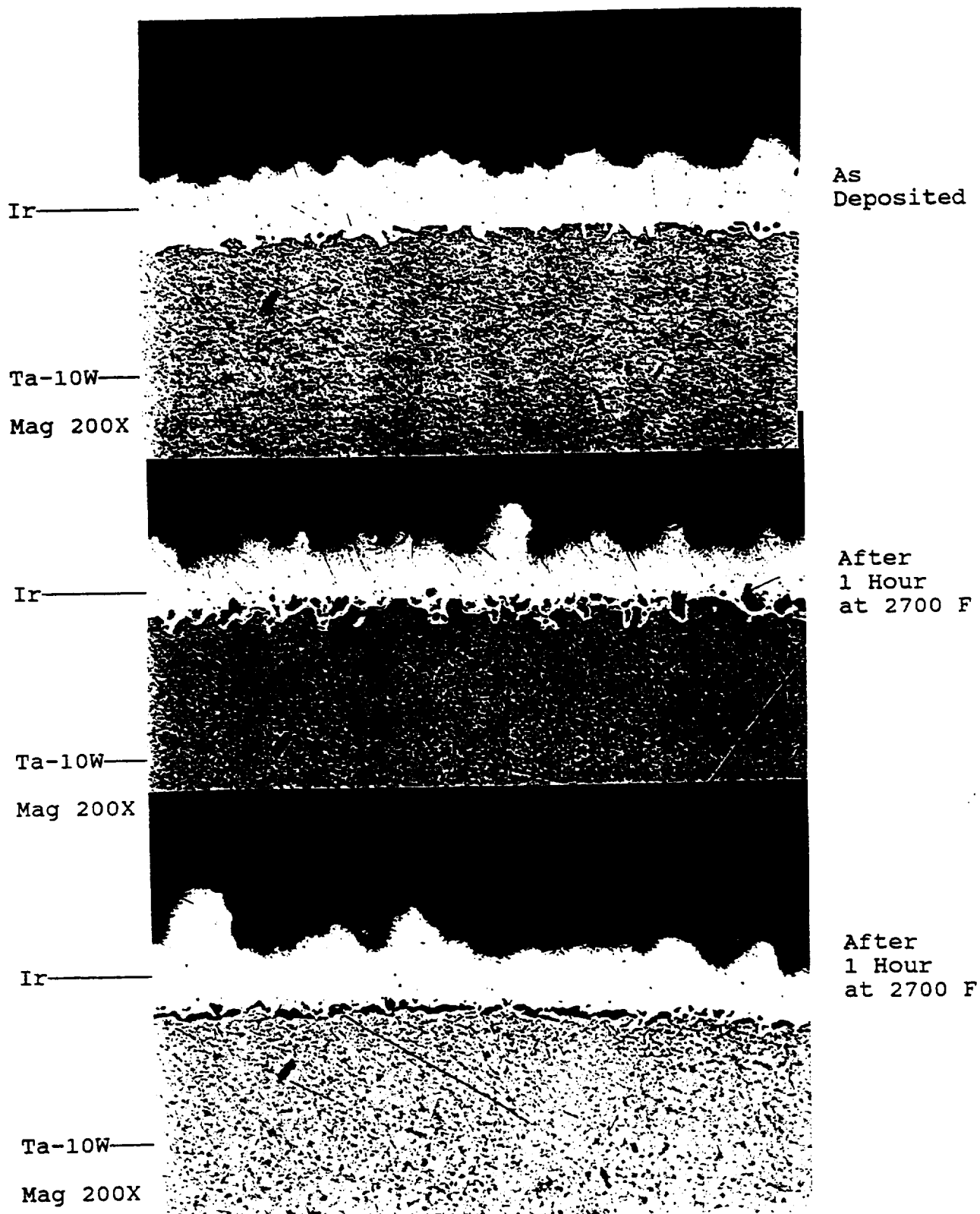


Figure 53. Formation of Kirkendall Voids at Interface Diffusion Region of Iridium Plated on Ta-10W Alloy.



when initial platinum group metal deposits on a refractory metal substrate are thin (under 25  $\mu\text{m}$ ), it is necessary to expose the part to hot concentrated acids for short times (under 30 seconds) to prevent pitting attack on the substrate. Soaks in hot water must be lengthened to assure removal of all salts.

### Conclusions and Recommendations

Refractory metal substrates can be activated to accept electroplated interfacial coatings of chromium or rhenium on which additional platings of platinum group metals can be made for oxidation protection. The chromium interfacial deposits should only be used where service temperatures are limited because of the low melting point of this metal compared with other materials in the coating system. Rhenium can be deposited in useful thicknesses for interfacial coating applications - particularly where diffusion of substrate and coating can result in Kirkendall voids. The rhenium needs further development, since hydrated oxides of rhenium are codeposited which lead to degradation of the coating into a powdery deposit. Relief from this problem can be achieved by heat treating the rhenium deposit in a reducing atmosphere such as hydrogen at temperatures of 1200°C and above. Ruthenium with a suitably high melting point might be used for interfacial deposits; however, its reaction to Kirkendall voids requires study.

Direct deposition of iridium, platinum, and rhodium can be made on all of the candidate refractory metal substrates examined in this work. High integrity bonds can be achieved providing the substrate metal is properly prepared by cleaning, deoxidizing (pickling), anodic etching (where required), and cathodic acid activation. Care must be exercised in selecting cathodic activation acids that are compatible with the plating strikes and solutions used to plate the platinum group metal. Multiple layering of platinum group metal coatings has been found beneficial in maintaining surface smoothness and allowing for rework by sanding and polishing to maintain a smooth coating profile. The multiple layering can be in the form of consecutive layers of the same metal or it can be in the form of alternating layers of two or more platinum group metals. Procedures have been developed and described whereby high integrity bonds are produced between these layers.

Work is still needed for examining in-process heat treatments at early stages of deposit build-up to consolidate and possibly diffuse the materials forming the substrate/coating interface. This is likely to decrease the risk of pitting and salt formation in pores existing at the early stages of coating and facilitate re-activations for continued deposition of thick coatings.

**TASK III - DEVELOPMENT OF ELECTRODEPOSITED MUTUAL ALLOYS OF THE  
PLATINUM GROUP METALS AND ALLOYS OF THE PLATINUM GROUP  
WITH OTHER REFRACTORY METALS  
PART A - DEPOSITION OF MUTUAL ALLOYS OF THE PLATINUM GROUP METALS**

**Background**

Little work has been reported in the literature on the deposition of mutual alloys of the platinum group metals - possibly due to the expense of the electrolytes and the difficulty in achieving thick deposits of commercial usefulness. Brenner [43] noted that three patents were assigned to Baker & Company covering the deposition of platinum, palladium, rhodium, and their alloys from ammino-nitrite salts. A platinum-rhodium alloy containing 90% of platinum was deposited from a bath containing 12.5 g/l of platinum chloride, 1.5 g/l of rhodium chloride, and 20 g/l of sodium nitrite. The bath required heating to 85°-90°C for a length of time to complex the solution to form a pale yellow color. In another patent granted to Precious Metals Development Company, the deposition of palladium-rhodium alloy was claimed.

**Deposition of Platinum-Iridium Alloy from Fused Salts**

Several specimens of Mo-47Re were platinum plated to thicknesses of 50 to 63  $\mu\text{m}$  (0.002-0.0025 in) from a fused salt bath. This bath was based on the sodium-potassium cyanide eutectic mixture used for iridium plating. The platinum was added to the melt by the use of 60 Hertz ac between two platinum electrodes. Platinum anodes were used with the bath and removed when no plating was being performed. These specimens appeared to have columnar grain growth and porosity was evident, so no high temperature oxidation testing was warranted. It was suspected that graininess had developed in the deposits due to the stainless steel fixturing being uncoated at the time this work was performed. Contamination of the melt would lead to rough grainy deposits.

Although investigation of mutual alloys of the platinum metals group had been considered in this study, the difficulties encountered in plating iridium from aqueous baths dictated use of the fused salt electrolytes. It was desired to include iridium in the alloy because of its very high melting point, and selection of platinum would promote better oxidation performance. Since both metals have been successfully deposited from the fused salt baths, it was considered expedient and sound to combine experience and technology for the two baths and create a blended melt.

Blending of the previous melts would appear the easiest approach. However, graininess and roughness encountered in late stages of use of the fused salt platinum bath dictated that a new melt should be prepared. Using the 70%-30% sodium to potassium cyanide

ratio, platinum and iridium were added by ac electrolysis of the anodes of these two materials. An ac electrolysis of platinum and iridium anodes for 22.4 hours resulted in a mass dissolution rate of platinum to iridium of approximately 5:1. In the first plating run of 3.25 hours at  $3.22 \text{ A/dm}^2$  (30 ASF) dc, the anode weight changes indicated the bath should be producing a deposit in the vicinity of 73% by weight iridium and 27% by weight platinum. A second plating run of 8.82 hours with pulsed current at a duty cycle of 50% and an average current density of  $1.08 \text{ A/dm}^2$  (10 ASF) produced a five fold increase in coating weight. Anode weight changes indicated a theoretical coating composition of 67% by weight iridium and 33% by weight platinum.

From an SEM probe analysis of the surface, Figure 54, the average coating composition of the platinum-iridium alloy deposited on Ta-10W was found to be 67.4% iridium and 32.6% platinum. A dark area, Area 1, was found to have a composition of 58.9% iridium, 31.2% platinum, and 11.2% iron. The iron was suspected to be a contaminant from the stainless steel fixturing which was uncoated in this study. Actual iron content on a coating mass basis was likely far less, since it was confined to nodular spots. Area 2 in Figure 54 analyzed as 73% iridium and 27% platinum.



Figure 54. Surface Scan of Iridium-Platinum Alloy Coating From Fused Salt Bath on Ta-10W Alloy Substrate. Arrows Represent Specific Locations of Localized Analyses. Magnification 200X. (Courtesy TRW, Redondo Beach, CA).

Further working of such a bath using periodic switching between separate iridium and platinum anode arrays should provide means

for selecting any alloy composition based on current flow ratios to the individual, anode arrays. Figure 55 is a photomicrograph of the iridium-platinum alloy on Ta-10W alloy. The coating appears continuous but rough.

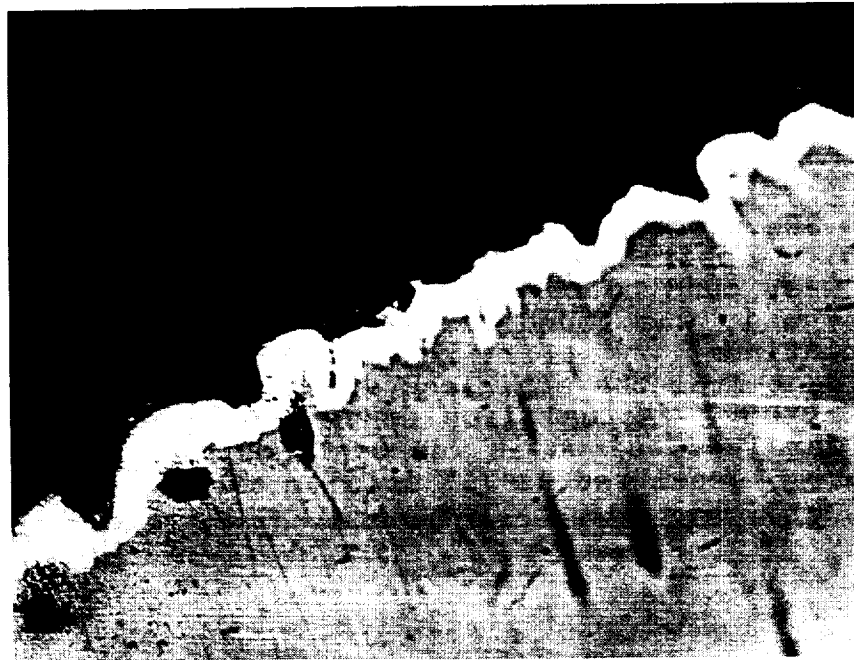


Figure 55. Metallurgical Evaluation Section of Iridium-Platinum Alloy Deposit on Ta-10W (Specimen No. 2). Magnification 400X.

#### Conclusions and Recommendations

Alloys of the platinum group metals iridium and platinum can be deposited with controllable compositions based on the findings of this investigation. Such alloys are currently produced only from the fused salt bath, since iridium is difficult to deposit from aqueous type electrolytes. Iridium is a desired element in any such alloys for high temperature use because of its high melting temperature. Rhodium alloys of iridium would be of interest, but rhodium is difficult to deposit from fused salt baths. Should it become possible to deposit iridium in thick, coherent forms from aqueous baths, it is recommended that investigation of rhodium additions - possibly in the form of trichlorides be performed.

**TASK III - DEVELOPMENT OF ELECTRODEPOSITED MUTUAL ALLOYS OF THE  
PLATINUM GROUP METALS AND ALLOYS OF THE PLATINUM GROUP  
WITH OTHER REFRACTORY METALS  
PART B - ALLOYS OF PLATINUM GROUP AND REFRACTORY METALS  
BY DIFFUSION**

**Background**

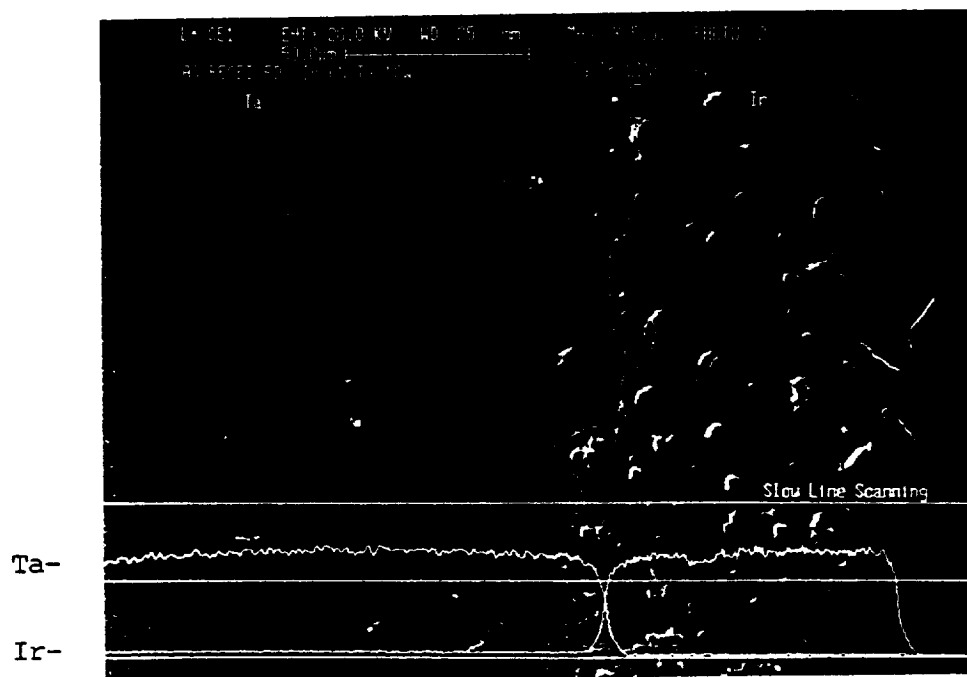
The purpose of this study was to determine if the electrochemical equivalents of Engel-Brewer compounds could be produced by thermal treatment of electrodeposited coatings of platinum group metals on selected refractory metal substrates. Such compounds are reportedly excellent from the standpoint of thermal stability and have very high melting points. This would be a valuable means of producing such materials, since the coating conforms to the part on which it is plated. This would simplify fabrication, provided the refractory substrate can be machined to the required shape.

**Diffusion Studies**

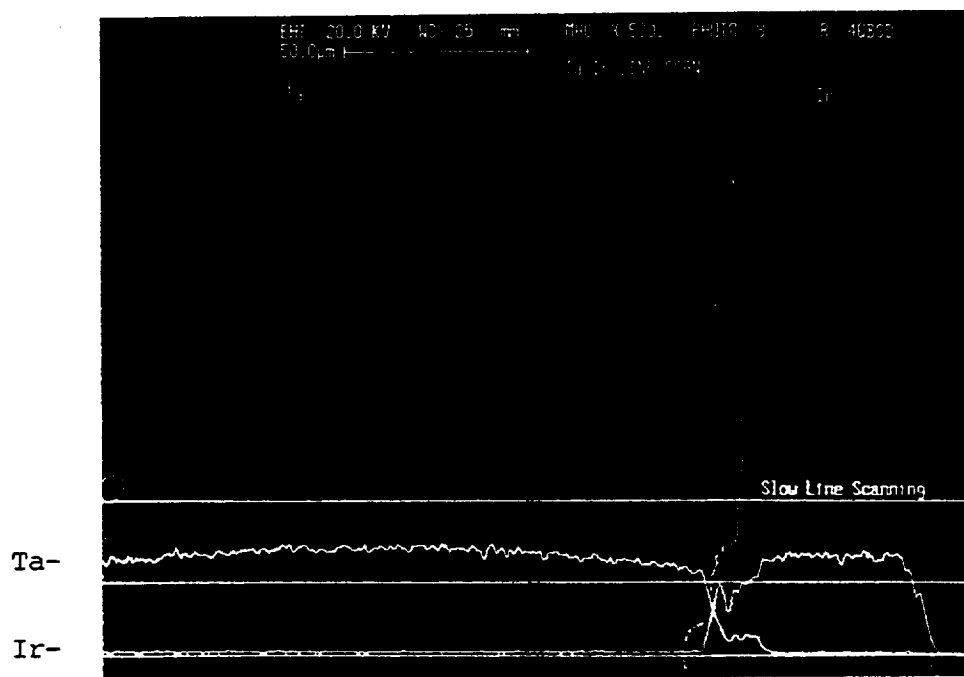
Since numerous substrates and coating combinations have been used in the prior tasks of this program, samples have been available for various heat treatments to determine adhesion characteristics and thermal stabilities. Results of these studies are presented at this time to illustrate anticipated effects from thermal diffusion on these combinations.

Substrates of tungsten have already been shown to block diffusion of platinum group metals, Figure 52. In this example, iridium was deposited on tungsten and heated in a vacuum for six hours at 1427°C (2600°F). The fact that the iridium was strongly bonded to the tungsten through this temperature excursion indicates an adhesion stronger than would be expected from mechanical means, and it may be assumed that some diffusion may have occurred on an atomic level. This combination would not lend itself to this method of producing Engel-Brewer compounds.

Figure 53 illustrates the exact opposite of the previous combination. In this example, iridium has been deposited on Ta-10W alloy and subjected to 1482°C in a vacuum for one hour. Diffusion was so rapid that Kirkendall voids formed. Continued treatment at high temperature can cause these voids to grow and combine to cause localized delaminations. However, elemental line scanning of this interface before and after thermal treatment shows the significant degree of diffusion that occurred in only one hour, Figure 56. Such a combination might prove useful in producing Engel-Brewer compounds if a means can be found to slow the diffusion to a more controlled rate - perhaps with a much lower temperature and longer times (or with the aid of hot isostatic pressurization). It might also be possible to slow diffusion by use of a very thin interface film of rhenium.



Elemental Line Scan of "As Deposited" Iridium Plated Ta-10W



Elemental Line Scan of Iridium Plated Ta-10W Interface After Heat Treatment at 1482 in Vacuum for 1 Hour.

Figure 56. Iridium and Tantalum Elemental Line Scans of the Diffusion Interface of Iridium Plated Ta-10W Before and After Heat Treatment at 1482°C in Vacuum for 1 Hour.

Figure 57 shows a cross-section of Ta-10W on which approximately 50  $\mu\text{m}$  (0.002 in) of rhodium was deposited in two stages. This material combination was vacuum heat treated at 1427°C (2600°F) for six hours. A rather thick diffusion zone appears to exist; however, the presence of Kirkendall voids is not readily apparent with this combination of metals. This was not expected based on the voids noted with Ta-10W and iridium. The cracks noted in the rhodium are expected for this thickness - considering that the optimum stress reducer system wasn't present in the rhodium plating bath. It is noteworthy that the cracks present in the initial rhodium layer have closed and healed as a result of the heat treatment. This appears to be the best candidate material system for producing Engel-Brewer compounds from an electrodeposit on a refractory metal.

A rhenium rod produced by powder metallurgy techniques was plated with iridium from a fused salt bath followed by an over plate of rhodium. Figure 58 shows elemental line scans of the elements composing this coating and substrate system in the "as deposited" and heat treated conditions. In the "as deposited" condition, the metal interfaces are noted to have a sharp demarkation. After heat treating at 1649°C (3000°F), the demarkation between the iridium and rhenium is not nearly as sharp, indicating slight diffusion. The interface between the iridium and rhodium shows a preferential diffusion of iridium into the rhodium. This system does not appear promising as a means of producing Engel-Brewer compounds on refractory metal surfaces.

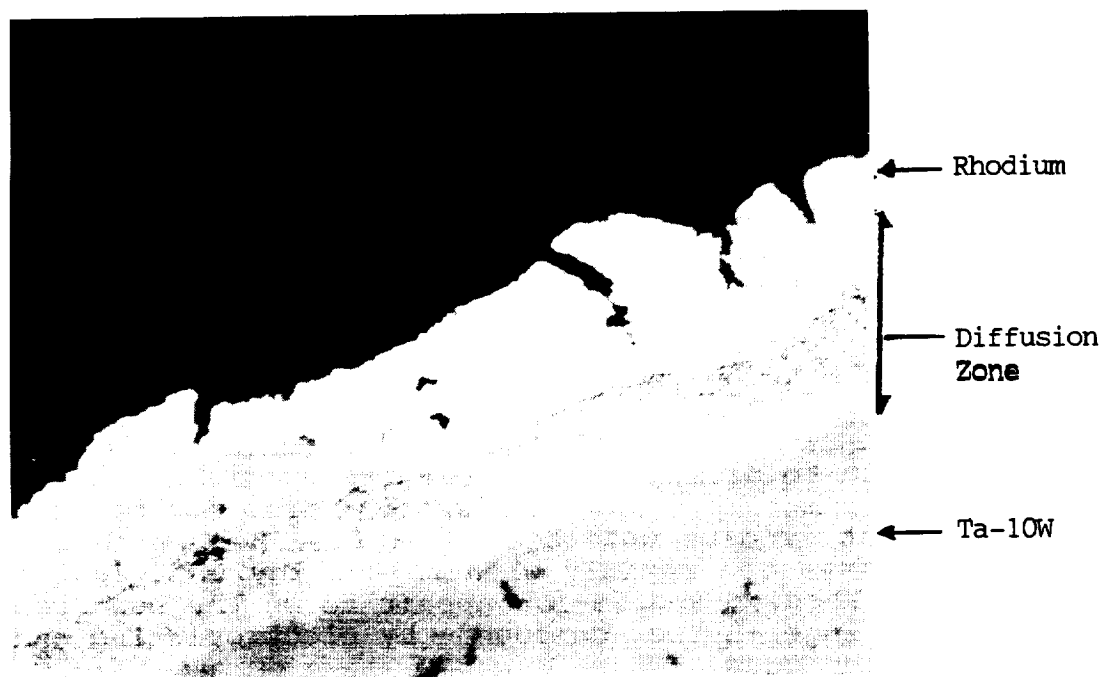
Deposits of iridium, platinum, and rhodium on Mo-47Re alloy have been heat treated and hot isostatic pressurized to 1538°C and as much as 20 ksi pressure to obtain diffusion for coating adhesion improvement. Although this has helped, there has not been significant diffusion zones established based on photomicrographs seen to date.

## Conclusions and Recommendations

Substrates with significant amounts of tungsten or rhenium are very resistant to diffusion with electrodeposited coatings of the platinum group metals. The same appears true for molybdenum. It was found that iridium and rhodium diffuse well with Ta-10W, but iridium diffuses too rapidly with this alloy and creates Kirkendall voids. Rhodium and Ta-10W appear to be the best combination for creating Engel-Brewer compounds by electroplating and thermal treatment techniques.



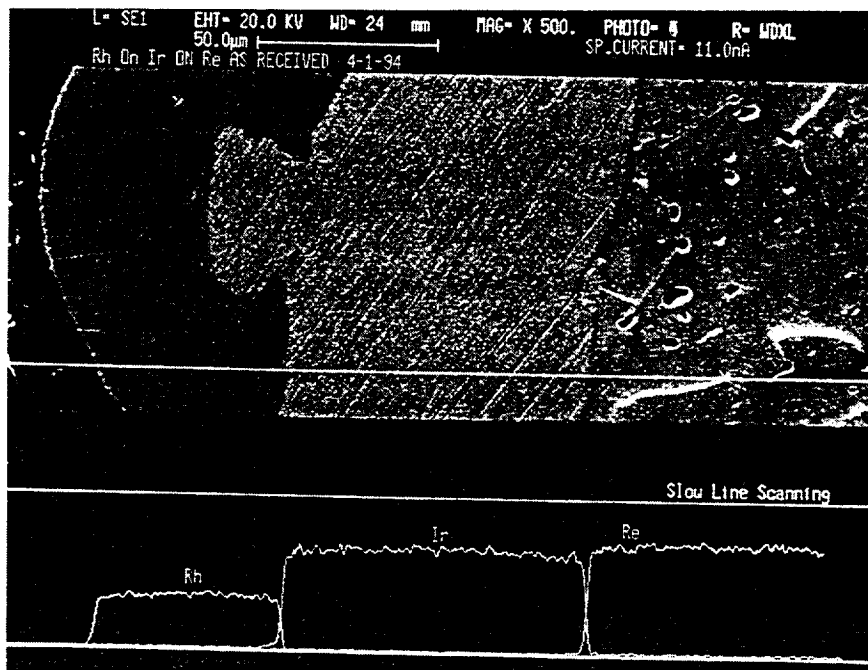
Microcracked Rhodium Electrodeposit on Ta-10W - As Deposited  
Magnification 200X. (Courtesy TRW, Redondo Beach, CA)



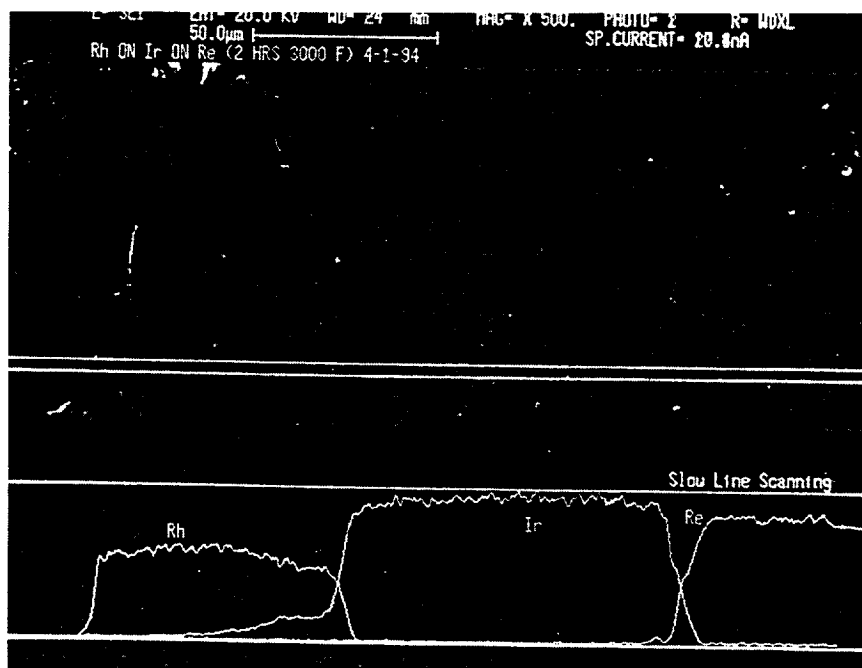
Rhodium Electrodeposit on Ta-10W After Heat Treatment at 1427°C  
for 6 Hours Showing Diffusion Zone. Magnification 400X.  
(Courtesy TRW, Redondo Beach, CA).

Figure 57. Effect of Thermal Treatment on Interface of  
Electroplated Rhodium on Ta-10W Substrate.





Elemental Scans of Electrodeposited Rhodium Over Iridium Over Powder Metallurgy Rhenium Rod, As Deposited. Magnification 500X.



Elemental Scans of Rhodium and Iridium Electrodeposits Over Powder Metallurgy Rhenium Rod After Thermal Treatment at 1649°C for 2 Hours. Magnification 500X.  
(Courtesy TRW, Redondo Beach, CA)

Figure 58. Rhodium, Iridium, and Rhenium Elemental Line Scans of the Diffusion Interfaces of Ta-10W Plated With Rhodium Over Iridium - Before and After Heat Treatment at 1649°C for 2 Hours.

**TASK III - DEVELOPMENT OF ELECTRODEPOSITED MUTUAL ALLOYS OF THE  
PLATINUM GROUP METALS AND ALLOYS OF THE PLATINUM GROUP  
WITH OTHER REFRACTORY METALS  
PART C - INVESTIGATION OF NONCONVENTIONAL METHODS OF DEPOSITING  
PLATINUM GROUP METALS AND ALLOYS**

**Aqueous Deposition of Platinum Group-Refractory Metal Alloys**

Difficulties in depositing sound deposits of rhenium from aqueous baths limited the investigations planned in this task. The co-deposition of hydrous, partly reduced oxides of rhenium severely limited deposit life in laboratory environments. However, some deposits were made from an acid rhenium chloride bath containing cobalt as an alloying additive, intended to facilitate rhenium reduction, were made. It would appear that cobalt (or nickel) reduces the hydrogen overpotential on such deposits leading to more hydrogen activity which aids rhenium reduction from the septavalent (+7) state. Cobalt contents were higher than desired, and the deposits were brittle and porous. Work with this alloy system is being pursued on a separate program with NASA-LeRC. It is expected that platinum group elements will be investigated on that program, if sound rhenium deposits are demonstrated.

**Nonaqueous Electrolytes for Platinum Group Metal Deposition**

Wakefield [44] reported work at Sandia National Laboratories in plating nickel, copper, and nickel-copper alloys from nonaqueous solutions composed of dimethyl sulfoxide, N,N-dimethyl formamide, and 1,2 ethanediol. These organic liquids are part of a group of polar molecules that can be used to dissolve certain metal halides and will conduct current. One advantage of such electrolytes is the absence of hydrogen in cathode reactions. Studies aimed at deposition of platinum group metals subject to significant hydrogen codeposition (i.e., rhodium) appeared worthwhile if stress could be reduced while plating coherent deposits.

Takei [45] examined deposition of tungsten, molybdenum, aluminum, and beryllium from organic solvents. He claimed deposition of aluminum and beryllium from trifluoroacetates, but molybdenum and tungsten deposits from phosphomolybdate and phosphotungstate baths contained codeposited oxides of the metals. Organic solvents used for the refractory metals were formamide, tetrahydrofuran, and N,N-dimethyl formamide.

In the present study the organic solvents investigated were ethyl benzene, propylene carbonate, toluene, dimethyl sulfoxide, and N,N-dimethyl formamide. Initial studies were directed at determining solubilities of iridium and rhenium salts in these solvents. Small vials were used which could be capped to prevent atmospheric moisture absorption by some of the solvents. Wires plated with gold were immersed in 20 ml quantities of the metal

salts in the solvent systems. Resistance measurements were made before and after additions of (1) complexing agents and (2) conductivity enhancing salts. Agents to complex iridium and rhenium ions were added and solubility evaluated visually. Conductivizing salts were then added and solubilization was again evaluated.

The iridium and rhenium salts were not readily soluble in the aromatic hydrocarbon systems such as ethyl benzene and toluene, so studies were confined to the aliphatic hydrocarbon solvents. A summarization of the solubility and conductivity investigations is found in Table XXI. Iridium and rhenium chloride salts were all quite soluble in dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF), propylene carbonate, and ethylene glycol. Thiocyanides and ethylenediammine tetra-acetic acid were also soluble as agents known to form complexes with these metals. Alkali and ammonium halides were sufficiently soluble to greatly improve the electrolyte conductivities.

Plating from scaled up electrolytes was conducted on copper test cylinders plated with nickel and gold as previously described for efficiency investigations in Task I. The first trial was with an iridium chloride concentration of 3.8 g/l in DMF using 2.5 g/l LiCl and 0.8 g/l LiBr for improved conductivity. Direct current was used with the current density ranging from 1.07 to 1.29 A/dm<sup>2</sup> (10 to 12 ASF). Platinized anodes were used. A dark gray metallic looking deposit was obtained which ignited on rinsing. This indicated the deposit to be lithium and not iridium. In a second trial, pulse plating was used with a 25% duty cycle, a peak current density of only 0.2 A/dm<sup>2</sup> (1.8 ASF), and an "on" time of 0.3 milliseconds and an "off" time of 0.9 milliseconds. Residues and cathode pitting were evident, but no iridium was deposited.

Another plating trial was made with 10 g/l of iridium chloride in propylene carbonate with chlorides and bromides present to improve conductivity, Specimen No. 56. Pulsed current was not used and the current density ranged from 0.11 to 0.17 A/dm<sup>2</sup> (1 to 1.5 ASF). The deposit appeared metallic gray near ends of the cylinder where current density was highest. Another trial, Specimen 66, was made a pulsed duty cycle of 10 percent, but no iridium deposit was obtained. Bath temperature was 70°C (158°F). It was noted that bath conductivity dropped as lithium was plated onto the cathode.

One scaled up trial to plate rhenium from a DMSO/DMF bath with 10 g/l rhenium chloride present and an addition of ammonium chloride and bromide for conductivity. With dc plating at 3.2 A/dm<sup>2</sup> (30 ASF), no rhenium deposit was obtained. Bath temperature during this trial ranged from 70° to 82°C (158° to 180°F).

#### Conclusions and Recommendations

No useful deposits from aprotic solvents were obtained.

TABLE XXI - SOLUBILITY AND CONDUCTIVITY STUDIES - ORGANIC BATHS

SAMPLE NUMBER AND METAL		SOLVENT A		SOLVENT B		METAL		SOLUBILITY OF METAL		ADDED COMPLEXER		SOLUBILITY OF COMPLEX		CONDUCT.		SOLUBILITY		INITIAL BATH		FINAL BATH		RESISTANCE VALUE	
		(ml)		(ml)		(grams)		SALT		(grams)		AGENT		(grams)		SALT		COLOR		COLOR		(Kilohms)	
01 Iridium	DMSO (20)	None		IrCl <sub>3</sub> (.2)		V. Soluble		None		None		N/A		None		N/A		Red-Black		Lt. Orange		36.00	
02 Iridium	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		None		None		N/A		None		N/A		Red-Black		Lt. Orange		22.00	
02A Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		None		None		N/A		KCl/XBr (1)		Part. Sol.		Red-Black		Lt. Orange		0.10	
03 Iridium	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		None		N/A		Red-Black		Lt. Orange		9.00	
03A Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		NH <sub>4</sub> Cl (1)		Part. Sol.		Red-Black		Lt. Orange		1.50	
03B Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		Sulfam. (4)		Part. Sol.		Red-Black		Lt. Orange		9.90	
03C Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		Saccha. (4)		Part. Sol.		Red-Black		Lt. Orange		9.00	
03D Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		LiCl (.4)		Part. Sol.		Red-Black		Lt. Orange		3.00	
03E Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		LiBr (.4)		Soluble		Red-Black		Lt. Orange		8.00	
03F Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		Am. Cit. (.4)		Part. Sol.		Red-Black		Lt. Orange		9.00	
03G Irid.	DMF (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		Cit. Ac. (.4)		Soluble		Red-Black		Lt. Orange		8.00	
23 Iridium	ProCar (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		Soluble		SCN- (.12)		SCN- (.12)		V. Soluble		None		N/A		Blk-Yellow		Blk-Yellow		Not Deter.	
23A Irid.	ProCar (10)	DMSO (10)		IrCl <sub>3</sub> (.2)		Soluble		SCN- (.12)		SCN- (.12)		V. Soluble		KCl+FormAc (1)		Pt Sol		Blk-Yellow		Orange		0.02	
24 Iridium	ethylene glycol (20)	None		IrCl <sub>3</sub> (.2)		Insoluble		EDTA (.2)		EDTA (.2)		Insoluble		None		N/A		Clear		Clear		Not Deter.	
20 Rhenium	DMF (20)	None		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		None		N/A		Dark Cherry		Green-Blk.		15.00	
20A Rhen.	DMF (10)	DMSO (10)		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		Am. Cit (1)		Part Sol.		Green-Blk.		Green-Blk.		0.10	
20B Rhen.	DMF (10)	DMSO (10)		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		Cit. Ac (1)		V. Soluble		Green-Blk.		Green-Blk.		11.00	
20C Rhen.	DMF (10)	DMSO (10)		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		NH <sub>4</sub> Cl (1)		Part. Sol.		Green-Blk.		Green-Blk.		6.00	
20D Rhen.	DMF (10)	DMSO (10)		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		NaCl (1)		V. Soluble		Green-Blk.		Green-Blk.		6.00	
20E Rhen.	DMF (10)	DMSO (10)		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		NaCl+KBr (3)		Pt. Sol.		Green-Blk.		Green-Blk.		5.00	
20F Rhen.	DMF (10)	DMSO (10)		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		NH <sub>4</sub> Br (1)		Part. Sol.		Green-Blk.		Green-Blk.		3.00	
20G Rhen.	DMF (10)	DMSO (10)		ReCl <sub>3</sub> (.2)		V. Soluble		SCN- (.05)		SCN- (.05)		V. Soluble		NH <sub>4</sub> Br+NH <sub>4</sub> Cl (1)		P. Sol		Green-Blk.		Green-Blk.		0.02	

**TASK III - DEVELOPMENT OF ELECTRODEPOSITED MUTUAL ALLOYS OF THE  
PLATINUM GROUP METALS AND ALLOYS OF THE PLATINUM GROUP  
WITH OTHER REFRACTORY METALS**

**PART D - INVESTIGATION OF NONAQUEOUS AND LOW TEMPERATURE MOLTEN  
SALT ELECTROLYTES FOR DEPOSITION OF REFRACTORY METALS**

**Background - Low Temperature Nonaqueous Melts**

There are several pyridene based inorganic compounds that become liquid at near room temperature. The electrochemistry of these "room temperature" molten salts has been under extensive investigation for at least 15 years. Gifford and Palmisano [46] studied the molten salt system prepared from aluminum chloride and a trialkylimidazolium chloride and found that molten salts prepared with this combination are stable over a wide compositional range at 25°C. The most widely studied system was aluminum chloride and N-butylpyridinium chloride, first reported by Robinson and Osteryoung [47]. Lipsztajn and Osteryoung [48] studied the behavior of iron, neodymium, and lithium in neutral ionic liquids composed of aluminum chloride and either N-1-butylpyridinium or 1-methyl-3-ethylimidazolium chloride. Aluminum metal has been deposited from such room temperature melts. Discussions [49] as to the possibility of substituting chlorides of other metals as a potential means of deposition were positive. This led to the use of iridium (III) chloride in the present studies.

**Facilities for Low Temperature Molten Salt Plating**

All of the organic salts forming the low temperature melt are extremely sensitive to air, because they are hygroscopic. Upon decomposition, they release carbon monoxide, nitrogen oxides, and hydrogen chloride gas. For this study a glove box was used with a separate entry compartment for transfer of chemicals and equipment. Argon or nitrogen purge capabilities were installed with a pressure relief valve for safety purposes. Modifications were made for electrical lead entries for power from externally located power supplies. The inert gas purge system was equipped with flow control valves and a flowmeter. Nitrogen or argon was supplied from high pressure cylinders. A separate inert gas purge was fed to the entry chamber. Accordion gloves were fitted to the hand entry ports on one side of the box.

Figures 59 and 60 illustrate the facility which contained a hotplate with magnetic stirrer, beakers, reagent containers, a laboratory scale, iridium wire anodes and copper wire cathodes, scrubbing media for cleaning wire contacts, and a thermometer. The imidazolium chloride compound was purchased from Aldrich Chemical, Milwaukee, WI. Since a good means of controlling temperature of the small vials used for initial plating studies was required, a ceramic container of glycerine was used on the hotplate as a heating jacket.

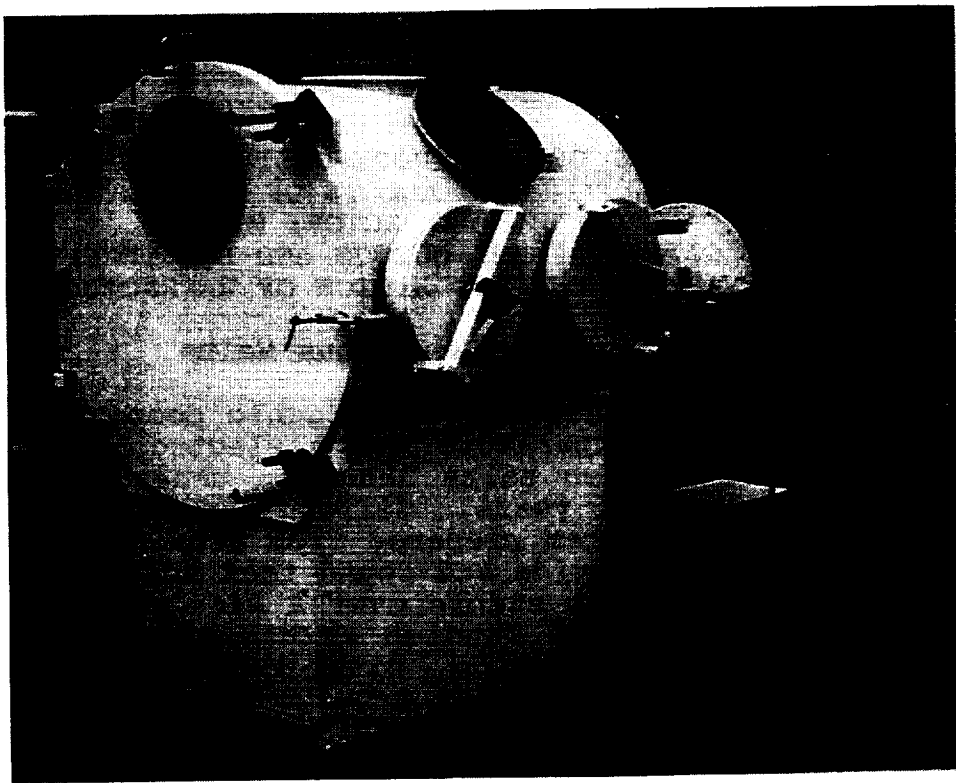


Figure 59. View of Inert Atmosphere Glove Box With Glove Ports Covered and Locked. Nitrogen Gas Feed Bottles Are in Background.



Figure 60. View of Glove Box Facility for Low Temperature Molten Salt Plating Showing the Entry Chamber and Inert Gas Feed Lines and Instrumentation.

## Imidizolium Chloride Bath Plating Studies

These polar low melting organic liquids perform as Lewis acids, and additions of soluble metal chlorides make the solutions more acidic in behavior. For this work, two molar ratios of iridium (III) chloride to imidizolium chloride were used -- 1:1 and 2:1. 4.91 grams of imidizolium chloride were melted in a vial by heating to 99°C. 10 grams of iridium chloride were added, and all of the salt dissolved. Initial plating was at a bath temperature of 85°C with direct current. No plating was observed on the copper wire cathode. A second plating run with a pulse setting of 0.3 msec on and 0.9 msec off failed to yield any iridium plating.

The ratio of IrCl<sub>3</sub> to imidizolium chloride was increased to 1.5:1 in the next plating trial. Direct current and pulsed current at duty cycles of 10% and 50% were used in that sequence. The gold plated copper cathode had a purple layer over the surface but no metallic deposit. The next study was performed on a melt with a ratio of IrCl<sub>3</sub> to imidizolium chloride of 2:1. Only direct current was used, and the cathode was gold plated nickel wire. The bath conductivity had decreased with the added iridium salts. No iridium was plated (the cathode had actually lost weight).

## Background - High Temperature Nonaqueous Melts

As an alternate means to deposit alloys of platinum group metals with refractory metals such as tungsten, the high temperature halide salt melts were investigated. Such baths are the only known electrolytes whereby tungsten or molybdenum can be deposited in a useful form and purity. Mellors and Senderoff [50] reported deposition of coherent tungsten from a fluoride eutectic melt. Their work forms the basis for the current investigation.

Based on prior successful work with plating platinum and iridium from cyanide melts, it appeared worth investigating such melts for plating tungsten. There were no references in the literature on which to weigh this decision. According to literature sources [51], there are tungsten cyanide compounds in which the valence of tungsten is +4 and +5. Senderoff [52] noted that tungsten is best plated in molten salt baths with a mean valence of 4.5, but his comments are appropriate to molten fluoride baths. In the present work the assumption was made that if tungsten electrodes could be electrochemically dissolved, a natural mean valence might exist by which reversing the electrochemical driving force would lead to coherent tungsten deposits.

## High Temperature Molten Salt Facility for Tungsten Studies

For the work with eutectic cyanide melts, the facility was that used in prior iridium and platinum fused salt plating studies. A blanket of argon was applied over the melt to prevent oxidation

of the melt and fixtures at the 600° to 650°C operating temperature of the bath. Operation was not in a glove box, since prior work with the cyanide melts indicated good stability with just a continuous argon purge. Upon changing over to a molten fluoride bath, the facility was incorporated into the glove box previously used in the imidizolium chloride studies. The floor of the glove box was cut open to seat a Mellen furnace and a small preheating furnace, Figure 61. Full view of the furnaces was provided by a clear acrylic panel which could be removed for servicing the furnaces. Electrical receptacles were also mounted in the acrylic for making power supply connections.

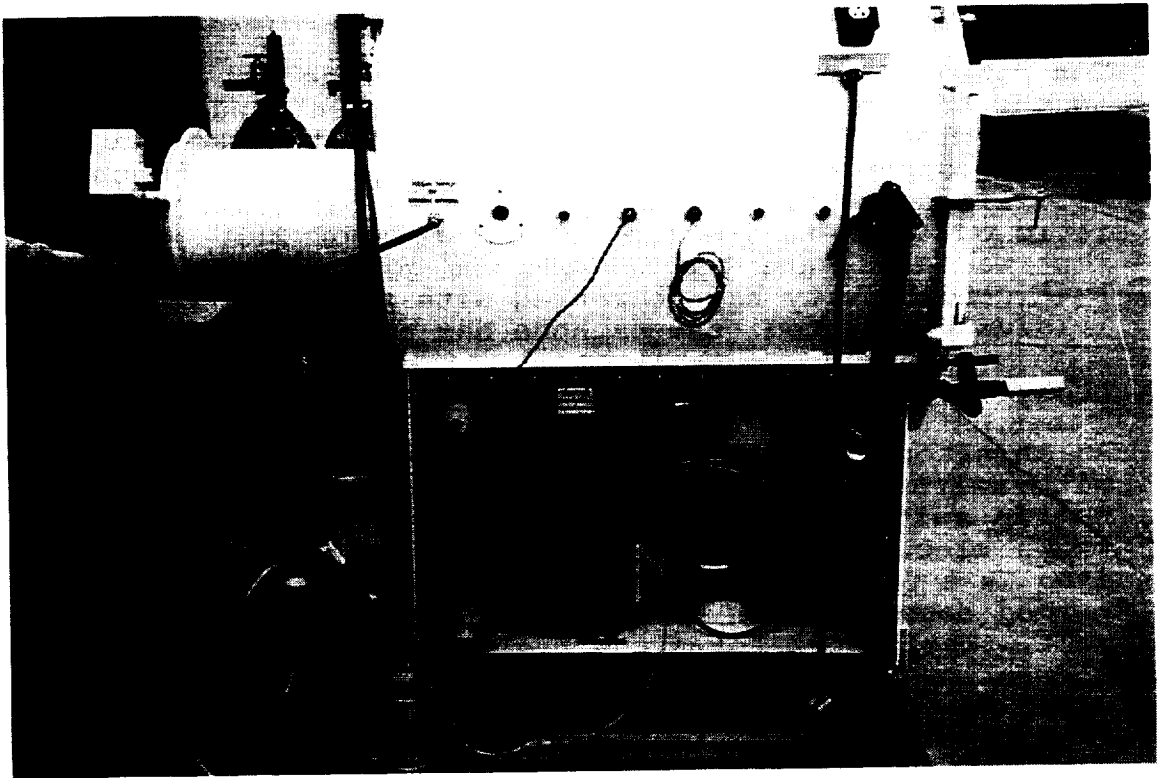


Figure 61. High Temperature Fused Salt Plating Facility.

A view of the interior of the glove box, Figure 62, shows the box opening to the furnaces, the furnace covers, furnace argon purge lines, and a probe thermocouple for measuring melt temperature.

#### High Temperature Fused Salt Studies - Cyanide Melt

The cyanide eutectic melt was produced by combining 70% by weight sodium cyanide with 30% by weight potassium cyanide for a total mix weight of 800 grams and heating the mixture to about 700°C. The melting point of this mix is about 585°C with the preferred operating temperature being about 620°C. There is a tendency for this mixture to form a crust and creep up crucible walls during melting, but increasing the temperature to 700°C melts the crust.



The melt was charged with tungsten by two methods: alternating current (ac) and direct current (dc) using broken CVD tungsten electrodes. Observations based on anode weight losses indicated that dc dissolved tungsten faster than ac, so the melt was mainly charged by dc. As tungsten was introduced to the melt, it appeared to striate at the bottom region of the crucible.

For the first plating trial, tungsten concentration in the melt was about 4 g/l. A Ta-10W rod cathode was processed as follows:

1. Weighed and dimensionally checked and recorded.
2. Degreased in acetone, air dried, cleaned in Oakite 90 with ultrasonics, and rinsed in deionized water.
3. Acid pickled in a room temperature solution of 28% by volume nitric acid, 16% by volume HF, 28% by volume sulfuric acid, and 28% by volume water for 20 to 60 minutes and rinsed in deionized water.
4. Rod was dried, weighed, and dimensions recorded.
5. Activated with cathodic treatment at  $27.2 \text{ A/dm}^2$  for 1 minute in a solution of 2 parts by volume of sulfuric acid and 1 part by volume water at room temperature, and rinsed in deionized water.
6. Dried and preheated in a separate molten cyanide bath to clean and preheat the rod to proper plating temperature.
7. Placed in tungsten fused salt bath and plated at  $2.1 \text{ A/dm}^2$  for 4.2 hours.

After cleaning the rod there were no signs of tungsten deposits. Two more trials gave the same results. Increasing the current density to  $4.8 \text{ A/dm}^2$  and plating for 2.5 hours also resulted in no tungsten deposit. In another trial, tungsten content of the bath was increased to about 6 g/l. No tungsten plated, and it was noted that the crucible had cracked and caused damage to the furnace refractory bricks and heating elements. At this point, work with the fused cyanide bath was discontinued.

#### High Temperature Fused Salt Studies - Fluoride Melt

For this work, the modified glove box was used to house the fused salt bath. The eutectic fluoride mixture was prepared based on a formula supplied in the Canadian patent of Mellors and Senderoff [53] as:

Lithium Fluoride	(LiF)	31% by weight
Sodium Fluoride	(NaF)	13% by weight
Potassium Fluoride	(KF)	56% by weight

The melting point of this eutectic is about 480°C; however, the recommended operating temperature with tungsten present in the melt is 600° to 900°C. High density alumina crucibles were used to contain the melt which is highly corrosive. A second containment crucible was used as a backup in event of breakage.

In the first tungsten melt, 1200 grams of fluoride eutectic mixture were heated slowly in a one liter alumina crucible to produce a liquid melt of about 0.5 liter. 0.5 amperes of direct current were passed between graphite electrodes in the melt in an effort to decompose any water of hydration from the salts which may have remained during melting. Before adding tungsten, the melt had a clear water-like appearance. Tungsten was charged into the bath by passing direct current between two tungsten electrodes for 63 hours. 47 grams of tungsten were added in this manner at an average current of 0.13 A/dm<sup>2</sup> (91.2 ASF). The color of the melt appeared gray and had a resistance of 1.25 ohms. The tungsten concentration (based on net electrode weight loss) was 4 percent by weight. Before plating could be started, both alumina crucibles cracked and spilled melt onto the bottom and sides of the furnace refractory lining.

It was suspected that the alumina backup and primary containment crucibles cracked due to excessive ramp-up rates. A new Mellen furnace with a larger bore diameter was used for the next trial with a different crucible combination. With the slow ramp-up, the melting took 24 hours. Tungsten charging was accomplished in 82 hours, and the melt contained 45 gram of tungsten. A Ta-10W rod was prepared as previously described and plated at 4.3 A/dm<sup>2</sup> (40 ASF) for two hours at a melt temperature of 565°C. After the run, the sample was observed to have a thick dark gray layer of salts or tungsten powder over the surface exposed to the melt. This layer was not truly bonded but was difficult to remove. A second run on the specimen (after cleaning and preplate processing) was made, and a layer of the same description was observed - although no measurable change in cathode weight was found.

A new Ta-10W rod was processed in this same melt using a pulsed current with a 9% duty cycle of 1 msec on and 10 msec off. Average current density was 4.3 A/dm<sup>2</sup> (40 ASF), the plating time was 3 hours, and the melt temperature was 608°C. The cathode had a powdery dark gray coating such as found on the dc plated samples. On the next run the pulse duty cycle was changed to 50% with "on" and "off" times of 100 msec. The peak current density for this run was 6.45 A/dm<sup>2</sup> (60 ASF), the plating time was 2 hours, and the melt temperature was 610°C. The rod appearance was identical to that of the previous trials; no cathode weight gain could be determined. This melt was also lost due to a cracked crucible at a melt temperature of 740°C and a furnace temperature of 1050°C. A further study of this system was not made on the basis that (1) no useful tungsten deposits were obtained, and (2) a development

of better crucible design and protection systems would be necessary from safety considerations.

### Conclusions and Recommendations

Although aluminum can be deposited from the low temperature organic melts, iridium of similar valence can not be suitably reduced. Although salts other than imidizolium chloride are available, it is believed similar results will be achieved. Iridium, like other platinum group metals, forms numerous complexes very readily. These complexes in imidizolium chloride may be too strong for reduction without decomposing the organic portion of the melt. It is not known if similar results would be obtained using iridium (IV) chloride, since reduction might be related to a valence state other than +3. It is also possible that aluminum chloride may be necessary in the melt to control Lewis acid or base behavior.

Deposition of tungsten from cyanide melts does not appear to be a viable process. It would appear that the tungsten in solution is not of the correct average valence, or the complex with cyanide is difficult to reduce at the cathode. Efforts to reproduce the results of Mellors and Senderoff using a fluoride eutectic melt did not yield coherent tungsten deposits. Equipment failures led to abandonment of further work with this system. However, it may prove rewarding to continue such studies with better designed crucible containment systems. Achieving an average valence for tungsten of 4.5 suggested by Mellors and Senderoff may be dependent on working the melt for long periods of time and studying the effects of tungsten metal exposure during idle periods on disproportionation of specific valences present in the bath.

## TASK IV - FABRICATION OF DEMONSTRATION HARDWARE

### Background

Requests for Phase III efforts were received well before completing the Phase II efforts of this program. There was an apparent need for oxidation barrier coatings on interior surfaces of small thrusters being developed for commercial and military satellites. Throughout this program attention was centered on the deposition of such coatings on the outside surfaces of small plates, rods, and tubes. Such devices present special problems in fixturing and anode placement to obtain the desired thicknesses of coatings in selected areas. Where high temperature fused salt baths are concerned, fixturing is of major concern. A rhenium liner for such a thruster was furnished by Aerojet Propulsion, Sacramento, CA, for evaluation of iridium plating as a production and rework process.

### Iridium Plating of Rhenium Thrustor Shells

Figure 62 is a photograph of a rhenium liner after extensive firings in which the iridium had been eroded away on the interior. The object of this demonstration was to deposit a new iridium coating on the interior with iridium being permitted on the outside surfaces to reduce oxidation of bare rhenium surfaces during hot firings. From an economic standpoint it was desired to keep exterior deposits thinner than those on the inside.

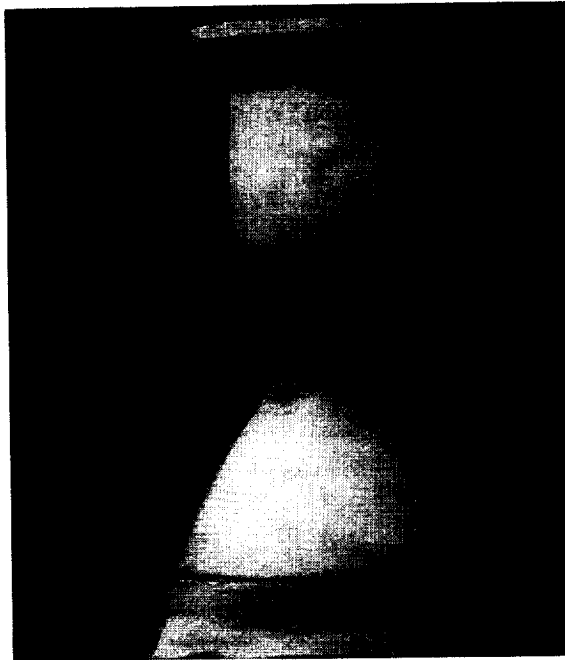


Figure 62. View of 100 Pound Uncooled Thrustor Shell to Be Plated With Iridium From a Fused Salt Bath.  
(Courtesy Aerojet Propulsion, Sacramento, CA)

This was the first experience with plating a part of this size in a fused salt bath. The furnace was a Mellen vertical (top loading) model with a 7 inch diameter by 6 inch depth heated zone. A Honeywell UDC-3000 controller capable of very slow ramping rates was used. The facility has been previously shown and described. The primary melt containment was in a two liter nickel-manganese alloy crucible that was electroformed. A Mullite crucible was used for secondary containment and electrical isolation of the metal primary crucible from the furnace wall and heating elements. The power supply was a Kraft Dynatronics Model DPR 20-30-100 with pulse and reverse pulse plating capability.

Figure 63 shows the fixture used to (1) rotate the cathode (in this case the part was not rotated), (2) provide argon inlet and outlet connections for purging, (3) hold and position internal anodes, and (4) provide electrical power to the plating cell. In cases where external anodes are used, a thick-walled ceramic tube is mounted above the containment crucible having stainless steel screws through the wall near the top for hanging anodes and making electrical contacts.

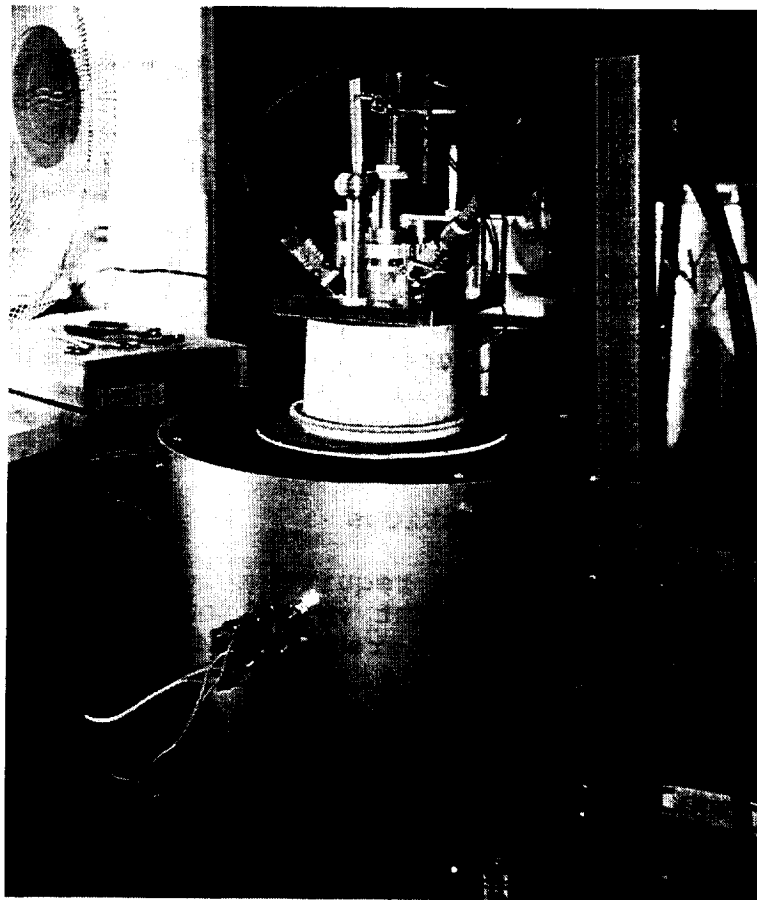


Figure 63. View of Fixture for Argon Purging, Part Suspension, Cathode Rotation, and Electrical Input for Fused Salt Plating.

Electrical contact to the rhenium thruster was provided by twisting a length of iridium wire around the outside of the throat and running it up the side for connection to the cathode lead from the power supply. A rectangular iridium anode was attached to the variable speed drive of the rotating fixture to enable centering in the interior of the part being plated. The thruster was prepared for plating by washing in Alconox detergent solution, rinsing, drying, soaking in acetone, and air drying. It was then preheated to about 600°C in argon in a small furnace.

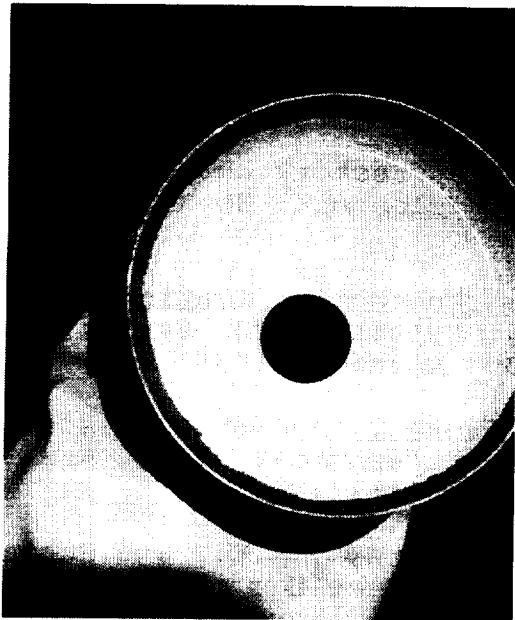
The part was inserted in the iridium melt with the nozzle end up for the first plating run. The injector end was seated on a dish made of alumina to provide an insulation from the metal crucible. The iridium anode was rotated to provide some stirring agitation to the iridium melt. The part was plated for 5.6 hours at a current density of approximately 1 to 1.5 A/dm<sup>2</sup> (10 to 15 ASF). The current density varied significantly due to the shape of the part and the fact that only an internal anode was used in the plating run. The iridium was adherent and completely covered the rhenium inside of the nozzle end. The chamber (injector) end was partially plated and thin because it was hidden from the anode.

In the second iridium plating run the thruster was inserted into the melt with the injector end up; the nozzle end rested in the shallow alumina dish at the bottom of the melt. The plating run was for 5.8 hours. The iridium was adherent and covered all of the rhenium inside the chamber section. However, a small area of rough rhenium near the throat required mechanical rework by sanding for subsequent plating in a third run. The third run was for 2.3 hours with the thruster immersed in the same attitude as used in the second plating run. The plating of the interior appeared successful, Figure 64. Because of the alumina dish insulator at the bottom of the melt, little iridium was deposited on the nozzle skirt beyond the attachment ring. This was not considered critical, so no additional runs were made to cover it.

### Conclusions and Recommendations

Although special crucibles require a long procurement lead time, the use of such a containment vessel of the right dimensions for the thruster would provide greater ease in plating and the part could be rotated for better iridium distribution. Use of a long interior iridium (or rhenium) anode extending through the throat of the thruster would assure better first stage plate coverage of the inside surfaces. The direct attachment of the thruster to an adaptor, which grips the part with a small contact area, would be beneficial in making quick connections to the cathode rotating spindle. Ability to rotate the part and internal anode would aid in melt stirring and more uniform plating. Use of a second melt would be helpful in building thick coatings, since the iridium plating efficiency appears to drop with time when one melt is

continuously used. Overall, the iridium plating of the 100 pound thruster appeared successful. As of this report, no test data has been furnished by Aerojet Propulsion.



Nozzle End



Injector End

Figure 64. Views of Aerojet Supplied 100 Pound Thruster After Iridium Plating Interior Surfaces From a Fused Salt Bath.

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